Hydroformylation of long chain olefins in microemulsion

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Abstract

Hydroformylation is one of the most important applications of homogeneous catalysis that is used in the production of aldehydes. The process which was developed by Ruhrchemie and Rhône-Poulenc (RCH/RP) is nearly optimized with respect to energy and material utilization. The catalyst is immobilized in water phase and immiscible with organic product phase. However, this process is not applicable to long chain alkenes due to their poor water solubility. This solubility problem can be solved by performing hydroformylation in microemulsion.

In this work we describe how addition of alkylpolygylcol ether type nonionic surfactant affects the hydroformylation of different olefins, namely 1-octene, styrene, cyclohexene, and 1,4-diacetoxy-2-butenе, in the presence of phosphine modified rhodium catalyst. Influence of different process parameters such as ligand excess and amount of surfactant on the reaction rate and selectivity were discussed.

Direct comparison of microemulsion systems with classic processes was achieved by performing the reactions under comparable homogeneous and biphasic conditions. Thus, the experiments were carried out using catalysts such as unmodified rhodium carbonyl $HRh(CO)_4$ and $HRh(CO)(PPh_3)_3$ in homogeneous system, $Rh-TPPTS$ complex in two phase system and in association with co-solvent.

In order to better understand the behavior and influence of microemulsion, active species of rhodium catalyst during hydroformylation was investigated by means of high pressure infra-red (HP-IR) spectroscopy. Formation of various rhodium carbonyl complexes was discussed.

Furthermore, another important aspect of rhodium catalyzed hydroformylation due to its high price, namely rhodium loss by organic phase was studied under biphasic and microemulsion conditions in a temperature range of 40-90 $^{\circ}C$.

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1 Introduction

Hydroformylation which is also known as oxo synthesis was discovered in 1938 by Otto Roelen. He detected this new chemical reaction when he aimed at increasing the chain length of Fisher-Tropsch hydrocarbons by passing a mixture of ethylene and synthesis gas over cobalt containing catalyst at 150 $°C$ and 100 bar in the laboratories of Ruhrchemie AG at Oberhausen, Germany [1].

In hydroformylation olefinic double bond react with synthesis gas (carbon monoxide and hydrogen) in the presence of transition metal catalyst to form linear (n) and branched (b) aldehydes containing an additional carbon atom as primary products (cf. Figure 1).

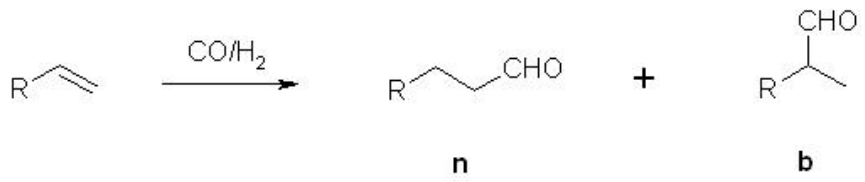

Figure 1: Hydroformylation of olefins.

Starting from mid 1950s hydroformylation gained an importance. In 1997 the total worldwide oxo production capacity was $6.5 * 10^6$ t/a for aldehydes and alcohols. Today hydroformylation is the largest scale application of homogeneous organometallic catalysis [2].

The most important oxo products are in the range C_3-C_{19}. The economic importance of oxo synthesis is mainly based on butanal with a share of 73 % of overall hydroformylation capacity. The n-butanal is converted to 2-ethylhexanol which is used in the production of dioctyl phthalate (DOP), a plasticizer that is used in the poly (vinyl chloride) (PVC) applications.

Industrially important oxo processes can be divided into five main types. Table 1 gives an overview of their catalyst system and reaction conditions. The most important of rhodium based processes on an industrial scale uses the so-called phosphine modified catalyst system. The unmodified rhodium carbonyl complex is used for the reaction of special olefins (Process 3). Because the reaction products consist of

Table 1: Industrially important oxo processes [3].

Catalyst metal	Cobalt		Rhodium		
Variant	Unmodified	Modified	Unmodified	Modified	
Ligand	None	Phosphines	None	Phosphines	
Process[a]	1	2	3	4	5
Active catalyst species	$HCo(CO)_4$	$HCo(CO)_3(L)$	$HRh(CO)_4$	$HRh(CO)(L)_3$	$HRh(CO)(L)_3$
Temp. ($°C$)	150-180	160-200	100-140	60-120	110-130
Pressure (bar)	200-300	50-150	200-300	10-50	40-60
Catalyst conc. rel. to olefin %	0.1-1	0.6	10^{-4}-0.01	0.01-0.1	0.001-1
Products	Aldehydes	Alcohols	Aldehydes	Aldehydes	Aldehydes
Amount of byproducts	High	High	Low	Low	Low
n/b ratio	80:20[b]	88:12	50:50	92:8	>95:<5
Sensitivity to poisons	No	No	No	Yes	No

a: key: 1 = (e.g.) BASF, Ruhrchemie; 2 = Shell; 3 = Ruhrchemie; 4 = Union Carbide (LPO); 5 = RHC/RP.
b: 65:35 at an early stage of development.

roughly equal amount of branched and linear aldehydes, this catalyst is only applicable if both aldehyde are valuable products or if the formation of the branched aldehyde is impossible (e.g., hydroformylation of ethylene to give propanal).

Up until the mid 1970s cobalt was used as catalyst metal in commercial processes (e.g., by BASF, Ruhrchemie, Kuhlmann). Because of instability of cobalt carbonyl, the reaction conditions were harsh with the pressure range of 200-350 *bar* to avoid decomposition of the catalyst and deposition of the metallic cobalt (Process 1).

The ligand modification introduced by Shell [4] researchers was significant progress in hydroformylation. The replacement of carbon monoxide with phosphines (or arsines) enhances the selectivity towards linear aldehyde (n/b) and the stability of cobalt carbonyl, leading to reduced carbon monoxide pressure (Process 2).

In 1974-1976 Union Carbide Corporation (UCC) [5] and Celanese Corporation [6], independently of one another, introduced rhodium based catalysts on an industrial scale. These processes combined the advantages of ligand modification with the use

of rhodium as a catalyst metal (Process 4). Because the reaction conditions were much milder, the process was called with the expression low-pressure oxo (LPO). Then low-pressure oxo (LPO) processes took the leading role and despite the higher price of rhodium, cobalt catalysts for the hydroformylation of propene has been replaced in nearly all major plants by rhodium catalysts. Higher price of rhodium was offset by mild reaction conditions, simpler and therefore cheaper equipment, high efficiency, and high yield of linear products and easy recovery of the catalyst. In addition, with respect to raw material utilization and energy conversation, the LPO processes were more advantageous than the cobalt technology, thus leading to their rapid growth.

In 1980s elegant solution with respect to catalyst recovery was offered by the Ruhrchemie / Rhône-Poulenc (RCH/RP) process (Process 5) [7]. Idea of two phase catalysis was applied to hydroformylation by using water soluble rhodium as a catalyst (cf. Figure 2). Trisulfonated triphenylphosphine ($TPPTS$, as sodium salt) as the ligand yields the water soluble catalyst $HRh(CO)(TPPTS)_3$. The biphasic but homogeneous reaction system exhibits distinct advantages over the conventional one phase processes [8]. Because of mutual insolubility, the separation of the aqueous catalyst phase and reaction products, including high-boiling by-products, is achieved most simply and efficiently.

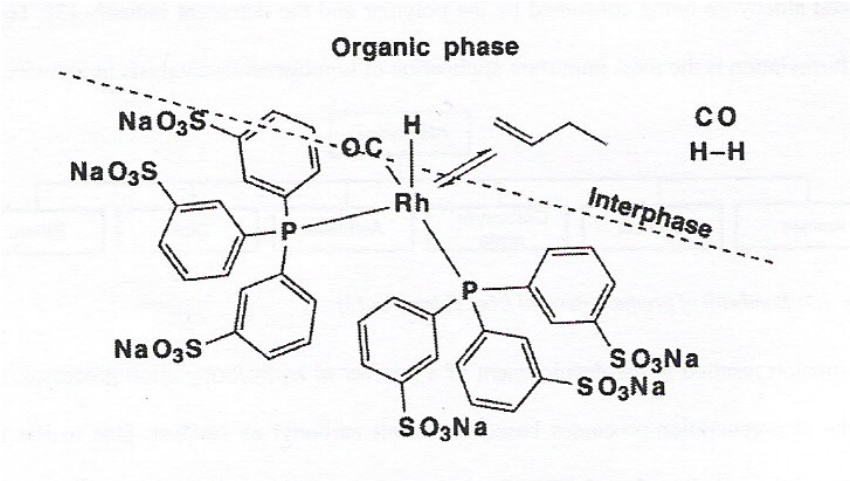

Figure 2: Two phase catalysis in the presence of water soluble rhodium complex.

However, the application of this process is limited to low molecular mass olefins

which have adequate water solubility [9]. The commercial hydroformylation of higher olefins (C_6 or larger) is performed exclusively with cobalt carbonyl catalyst. Several approaches have been developed for the hydroformylation of high olefins: (1) anchoring of rhodium catalyst to resins, polymeric or mineral support [10] [11]; (2) homogeneous catalyst with amphiphilic complexes which can be extracted in another phase at the end of the reaction [12]; (3) aqueous organic biphasic catalyst involving use of particular ligands [13], co-solvent [14] or cyclodextrin [15]; (4) supported hydrophilic liquid phase [16] or aqueous phase [17] catalysis.

One approach for the hydroformylation of long chain olefins is a performing the reaction in microemulsion. When water is mixed with olefin and a suitable amphiphile, optically transparent and thermodynamically stable mixture is obtained. The term microemulsion is used for this stable mixture. Their characteristic property is a large interfacial area between oil and water phases, thus solving the solubility problem of biphasic catalysis. By association of polar head groups of amphiphiles with colloidal drops of water in organic medium reverse micelles are formed. These reverse micelles carry catalytically active groups and act as a catalyst (cf. Figure 3). In microemulsion separation of catalyst and products can be achieved by simple phase separation as in biphasic catalysis.

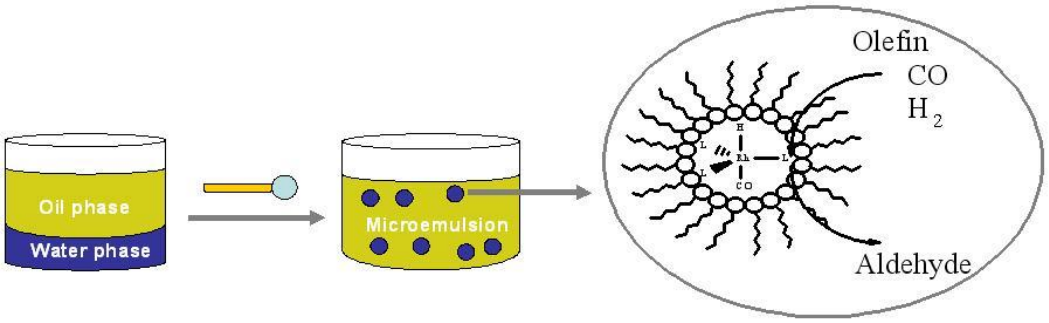

Figure 3: Principle of hydroformylation in microemulsion.

The main objective of this work is the investigation of microemulsion system as a reaction media in the hydroformylation of different olefins. Effect of nonionic surfactant on the rate and selectivity of the hydroformylation will be studied in the presence of phosphine modified rhodium catalyst. Direct comparison of microemul-

sion with the classical hydroformylation systems will be achieved by performing the reactions under comparable homogeneous and biphasic conditions.

Characterization of the intermediates present during the reaction is important aspect of the rhodium catalyzed hydroformylation. In order to better understand the behavior of microemulsion, formation of the various rhodium carbonyl complexes under microemulsion conditions will be investigated by means of high pressure infra-red (HP-IR) spectroscopy.

Another important aspect of the hydroformylation is the total recovery of catalyst due to high price of rhodium metal. Rhodium loss by the organic phase after phase separation will be discussed under microemulsion and biphasic conditions at various temperatures.

2 Theory

2.1 Hydroformylation

2.1.1 General Principles

Compounds of several transition metals catalyze hydroformylation to some extent, but the main interest lies in catalysis by cobalt or rhodium compounds. On the other hand platinum and ruthenium catalysts are mainly subjects of academic interest, not thoroughly investigated by industrial researchers. The generally accepted order of hydroformylation activity for unmodified monometallic catalysis is as follow [18]:

$$\text{Rh} \gg \text{Co} > \text{Ir, Ru} > \text{Os} > \text{Pt} > \text{Pd} > \text{Fe} > \text{Ni}$$

Hydroformylation with bi- and polymetallic catalysts have been several times studied [19]. These studies have shown that clusters are degraded to at least bimetallic species under hydroformylation conditions. Garland and co-workers [20] showed that in hydroformylation condition multinuclear complexes such as $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, and $Rh_2(CO)_4Cl_2$ are degraded to $HRh(CO)_3$ which performs the reaction.

A typical hydroformylation catalyst can be represented by structure

$$H_xM_y(CO)_zL_n$$

where M and L are metal atom and ligand, respectively. When n = 0, catalysts are called unmodified. Coordination of the metal center by ligands other than CO or hydrogen are designated modified.

Huge number of ligand applications appear in the area of hydroformylation, however the only classes of ligands used in industrial hydroformylation plants are phosphines PR_3 ($R = C_6H_5$, n-C_4H_9), triphenylphosphine oxide ($TPPO$) and phosphites, $P(OR)_3$ [3]. Nitrogen substituted ligands have attracted some interest in oxo research. Shell has submitted a patent application using phosphinoamines for the rhodium catalyzed hydroformylation of 2-propen-1-ol and 3-buten-2-ol [21]. However, in general nitrogen containing ligands such as amines, amides, or isonitriles showed low reaction rates due to their strong coordination to the metal center.

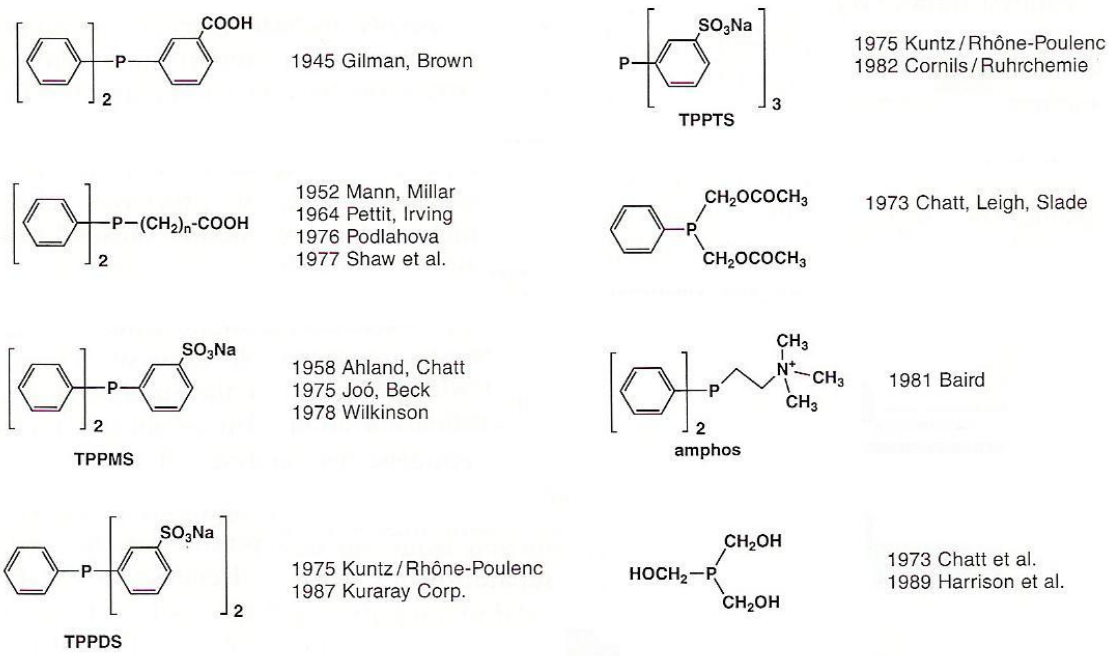

Figure 4: Water-soluble ligands for oxo homogeneous catalysts.

Rhodium-triphenylphosphine oxide ($TPPO$) is used in the production of isononanol by hydroformylation of octenes [22]. This is the only example known of an oxidized phosphine ligand on an industrial application. Rhodium catalysts with phosphites are used in the hydroformylation of long-chain olefins due to their high catalytic activity [23].

After the application of biphasic homogeneous catalysis on an industrial scale, the work on water soluble ligands gained importance. The solubility in water is usually achieved by introduction of highly polar substituents such as $-SO_3$, $-COOH$, $-OH$, or $-NH_2$ into the phosphine ligands [24]. Figure 4 shows the various water soluble ligands for oxo homogeneous catalysts. By variation of nature and number of suitable substituents and by choice of the conditions of aqueous phase, almost any desired ratio of hydrophobic and hydrophilic properties may be obtained.

The water soluble ligand tris-3-sulphophenyl-phosphine trissodiumsalt ($TPPTS$) can be prepared by the sulfonation of triphenylphosphine (TPP) with oleum (i.e., concentrated sulfuric acid containing 20 % by weight of SO_3) at 40 $°C$ in one day (cf. Figure 5). An aqueous solution of sodium sulfate with a mixture of TPPTS

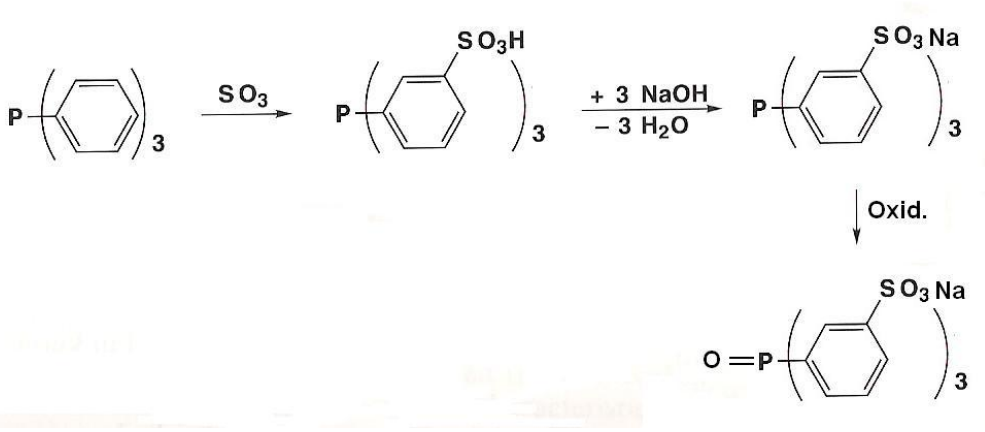

Figure 5: Synthesis of triphenylphosphine trisulfonate ($TPPTS$).

(mainly) and the corresponding phosphine-oxide are obtained after hydrolysis and neutralization by NaOH [25].

2.1.2 Mechanism of Hydroformylation

Mechanism of the oxo synthesis is still under investigation and has not been clarified in every detail [26]. Several differences in hydroformylation mechanism are observed between modified and unmodified systems. Therefore it will be useful to discuss them separately.

Unmodified Catalysts The mechanism for hydroformylation developed by Heck and Breslow for cobalt catalyst in the early 1960s [27]. The mechanism can be applied to unmodified rhodium complexes as well.

Catalytic cycle of hydroformylation with unmodified cobalt catalyst is shown in Figure 6. The hydroformylation cycle consists of seven elemental steps. The reaction of the metal carbonyl $Co_2(CO)_8$ with hydrogen to form the hydridometal carbonyl species $HCo(CO)_4$ (step 1) is followed by dissociation of CO to generate the unsaturated species $HCo(CO)_3$ (step 2). Coordination of an alkene to this unsaturated square planar complex (step 3) and hydride migration result in the formation of alkylmetal carbonyl species (step 4). After coordination of CO (step 5), insertation of CO occurs to give the acylmetal carbonyl complex (step 6). Hydrogen is added to this unsaturated acylmetal species and the catalytic cycle is completed with the

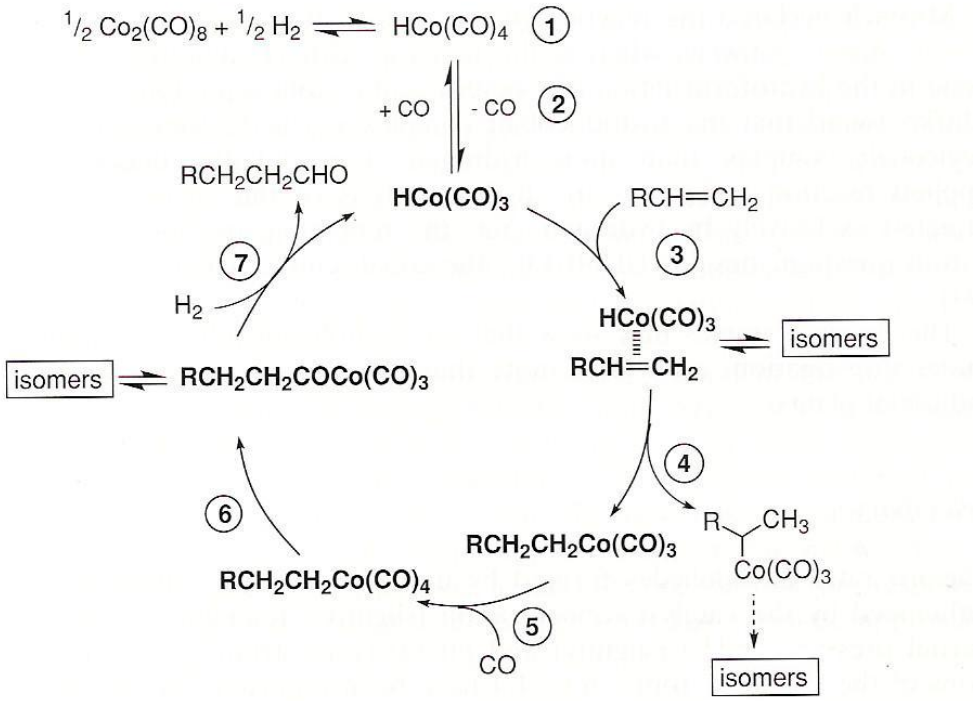

Figure 6: Catalytic cycle of hydroformylation for unmodified cobalt catalysts.

regeneration of active species $HCo(CO)_3$ and the formation of aldehyde (step 7).

Phosphine Modified Catalysts Introduction of phosphine ligand into catalytic system brings some critical changes. $HRh(CO)(TPP)_3$ is believed to be the precursor of the active hydroformylation species. Model studies with this hydride complex were provide explanation for different reaction behavior and indicated extensive dissociation of this complex. This means equilibrium exists between various substituted rhodium complexes before the catalytic cycle occurs (cf. Figure 7).

Each catalytic species is assigned an individual reaction rate and a characteristic product distribution. For example high phosphorus rhodium ratio and low partial pressure of carbon monoxide favor $HRh(CO)(L)_2$ complex which is assumed to give high linear aldehyde ratio (n/b) as a result of steric effects.

The mechanism for hydroformylation developed by Heck and Breslow for unmodified cobalt catalyst is valid with minor modification for phosphine modified rhodium catalysts. The catalytic cycle for phosphine modified rhodium catalysts was estab-

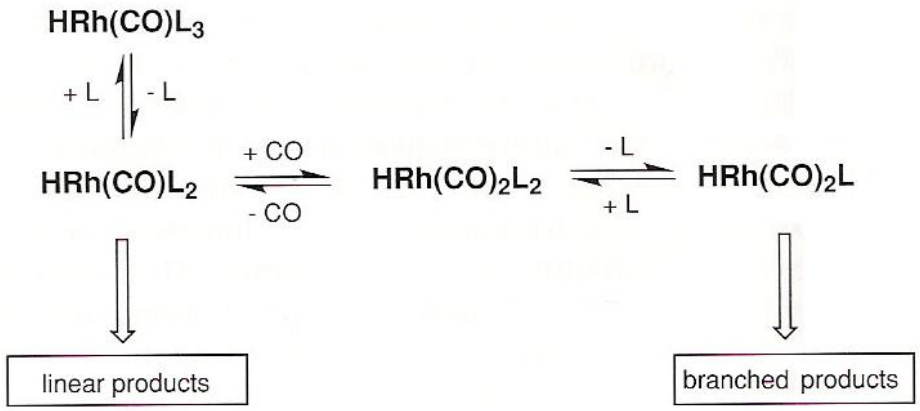

Figure 7: Initial equilibria forming the active species, L = TPP or $TPPTS$.

lished by Wilkonson with two possible path ways, the associative and the dissociative mechanisms [28]. Both mechanisms start with five coordinated bisphosphine complex $HRh(CO)_2(TPP)_2$, but differ as regards the primary reaction step, coordination of olefin to the rhodium center (cf. Figure 8).

In associative mechanism (route A) olefins attach directly to the bisphosphine species, and after hydride migration step alkylrhodium complex is obtained which is an intermediate of dissociative mechanism as well.

In dissociative mechanism (route D) two different coordinatively unsaturated complexes $HRh(CO)(TPP)_2$ and $HRh(CO)_2(TPP)$ can be formed by dissociation of CO or phosphine. Addition of alkene to this unsaturated complex (step 1) is followed by hydride migration (step 2). After coordination of CO (step 3), insertion of CO (step 4) occurs to give a rhodium acyl complex. The unsaturated rhodium acyl complex undergoes hydrogenolysis (step 5) and completes the catalytic cycle with the regeneration of active species and the production of either the linear or the branched aldehyde.

Dissociative mechanism is generally accepted under industrial operating conditions. The active species in this mechanism are unsaturated rhodium complexes containing one or two coordinated phosphine ($HRh(CO)_2(TPP)$ or $HRh(CO)(TPP)_2$) formed by dissociation of phosphine or CO. It is widely believed that the n/b ratio of the

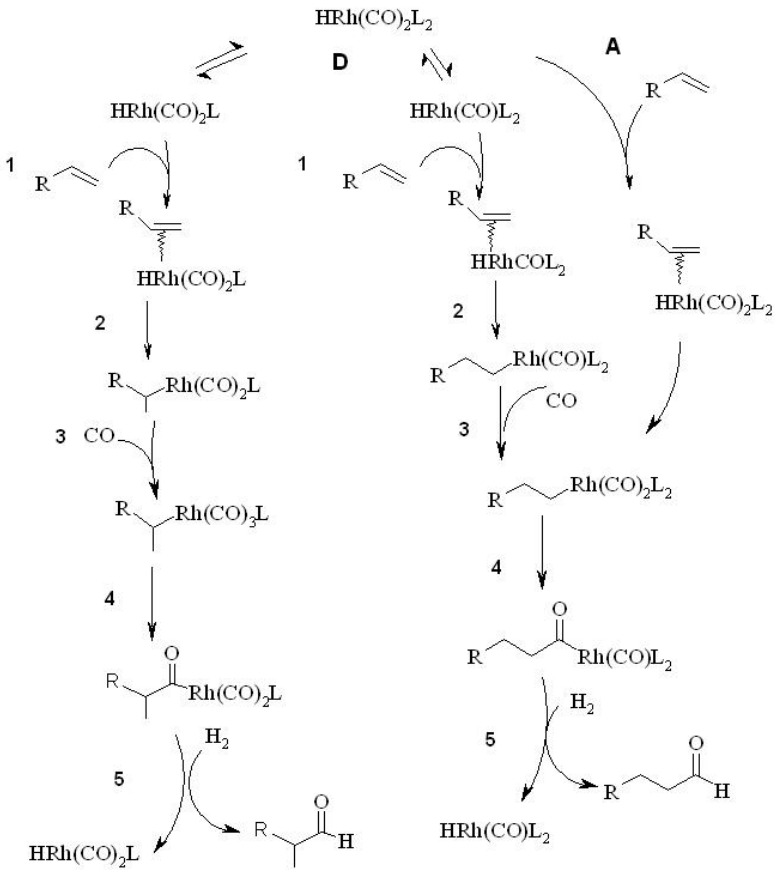

Figure 8: Catalytic cycle of hydroformylation for phosphine modified rhodium catalysts.

reaction is largely controlled by the competitive reaction of olefin with these unsaturated complexes. As a result of steric effect the species $HRh(CO)_2(TPP)$ would be responsible for the formation of the branched aldehyde whereas $HRh(CO)(TPP)_2$ would be responsible for the formation of linear aldehyde (see Figure 8).

However, remarkable differences were observed between the catalytic activity and the selectivity of the water soluble catalyst $HRh(CO)(TPPTS)_3$ and organic soluble one [29]. In the hydroformylation of propene the latter shows much lower activity with an increased selectivity to linear products. This is explained by the high dissociation energy (30 $kcal/mol$) of $TPPTS$ from $HRh(CO)(TPPTS)_3$. This energy is about 10 $kcal/mol$ higher than that necessary for dissociation of TPP. The lower catalytic activity might be due to higher dissociation energy. On the other hand because of high dissociation of TPPTS, the equilibrium between active species shifts towards unsaturated complex with two phosphine ligand, thus leading higher linear

aldehyde ratio (n/b).

2.1.3 Kinetics of Hydroformylation

Although hydroformylation has been studied in every detail, only a few repots on kinetic aspects have been published. Most of these works are on macrokinetic influences, e.g., temperature, pressure, synthesis gas composition and catalyst concentration. Generally conclusions about the rate determining step have been deduced from spectroscopic observation.

The rate equation under high synthesis gas pressure for unmodified oxo catalysts $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ has been derived by Natta and Ercoli [30].

$$r = k * [substrate] * [catalyst] * \frac{[p(H_2)]}{[p(CO)]} \tag{1}$$

The reaction shows a positive dependency on catalyst concentration, olefin and hydrogen, whereas carbon monoxide exerts a negative effect. However, at low carbon monoxide partial pressures (p(CO) $< 10\ bar$) a positive order dependency of the rate is observed, as the hydridocobalt carbonyls $HCo(CO)_3$ are stabilized. At higher carbon monoxide partial pressures, the less reactive $HCo(CO)_4$ is formed, therefore explaining the negative order of reaction. Unmodified rhodium catalysts behave the same way.

Many studies on the reaction kinetics and the resting state of an unmodified rhodium carbonyl catalyst using various substrates have been performed. Using hept-1-ene, under the typical reaction conditions of p(H_2) = 33-126 bar, p(CO) = 40-170 bar, T = 75 $°C$, the kinetic expression is the following [31],

$$r = \frac{k * [Rh] * [H_2]}{[CO]} \tag{2}$$

The reaction of hydrogen with the rhodium acyl intermediate is the rate determining step. At these high pressures, the reaction is inhibited by CO. At low CO pressures, the reaction is first order in CO concentration, the coordination of CO

to the rhodium alkyl complex now appearing as rate limiting.

For an internal olefin like cyclohexene and $Rh_4(CO)_{12}$ as the catalyst precursor, the rate expression reported by Marko [31] is

$$r = k * [cyclohexene] * [Rh]^{0.25} * [H_2]^{0.5} \tag{3}$$

From the infrared data, it was concluded that the addition of cyclohexene to the hydridorhodium carbonyl is rate determining.

For phosphine modified rhodium catalyst $HRh(CO)(TPP)_3$, the reaction rate is in first order with respect to catalyst concentration and hydrogen partial pressure. Substrate and CO inhibition appear at high olefin concentration and at highCO partial pressure, respectively. In addition, the rate is positively influenced by increasing in the concentration of ligand at low ligand concentrations whereas no dependence on ligand concentration is observed at high ligand concentrations.

Despite its importance, very few kinetic studies have been performed on water-soluble catalyst $HRh(CO)(TPPTS)_3$. The hydroformylation of 1-octene using water-soluble $Rh - TPPTS$ catalyst has been investigated in a temperature range of 353-373 K by Bhanage [32]. The rate of reaction was found to be first order with respect to catalyst concentration and hydrogen partial pressure. The rate determining step is the addition of hydrogen to acyl carbonyl rhodium species. In contrast to the CO inhibition observed for homogeneous catalyzed hydroformylation, the rate is in 0.7th order with CO. The formation of di- and tri-carbonyl rhodium species which is believed to be responsible for negative order dependence is not observed because the concentration of dissolved carbon monoxide in the water phase is very low compared with that in the organic phase.

2.1.4 Industrial Rhodium Based Processes

Low Pressure Oxo Processes (LPO) Thermal stability of rhodium phosphine complexes, even in the absence of carbon monoxide, allows working in lower synthesis gas pressures. Therefore these processes are called low pressure oxo (LPO). The LPO

technology was promoted by number of companies, mostly in parallel (e.g., Union Carbide, BASF, Mitsubishi). One of the first plant for butanal production belonged to Union Carbide Corporation (UCC) [33].

UCC Process The basic idea is to retain the catalyst in the synthesis reactor and to separate catalyst and product by distillation under reaction conditions [34]. The catalyst is soluble in high-boiling condensation products. These condensation products are principally un-wanted by products. Because the steadily increasing amount of high-boiling substances, their level has to be kept constant by intermittently or continuously separating catalyst and ligand from the high boilers in an additional process step [5]. Gaseous product (butanal) is removed by a huge gas stream (gas recycle process) from the reaction zone, thus complicates the overall process.

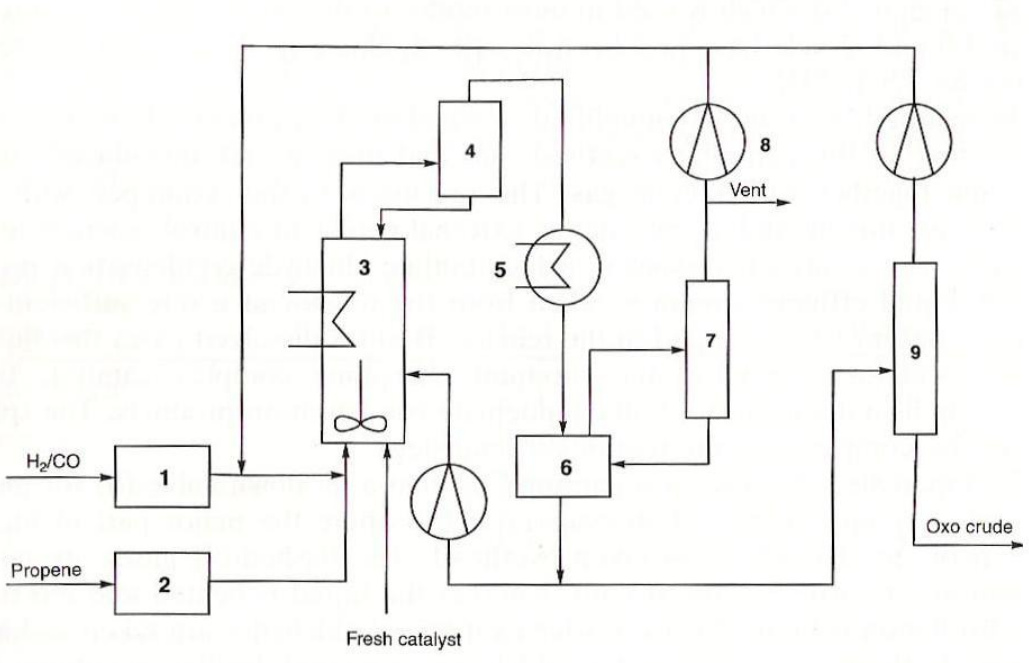

Figure 9: UCC process, gas recycle.

Layout of UCC gas recycle process is shown in Figure 9. Propene and make-up synthesis gas are purified (1, 2) and, together with recycle gas, introduced into the stainless steel reactor (3) via a sparger. The stirred reactor is equipped with an

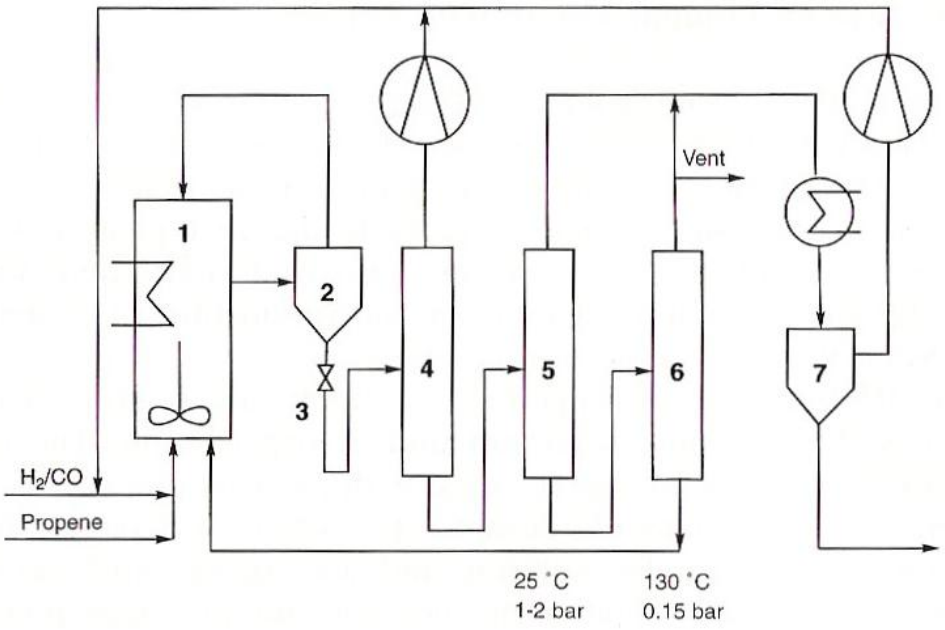

Figure 10: UCC process, liquid recycle.

external heating jacket (for start-up) and internal cooling coils. Effluent product vapor passes demisting pads (4) to prevent carry-over of catalyst and liquid products. Part of the gaseous aldehyde is condensed in a cooler (5) and collected in a separator (6), from which the recycle gas leaves via the demister (7) to the recycle compressor (8). A slipstream is taken to vent. Part of the condensed aldehyde from separator (6) is recycled to the reactor to keep the level of liquid constant. The main stream of crude oxo products is sent to the upgrading section [35].

In order to avoid the huge gas recycle which leads to fairly complex plant equipment, the gas recycle was replaced by the liquid recycle variant (Figure 10).

A liquid effluent stream that is taken from the reactor contains aldehydes, the rhodium phosphine complex, free ligand and high boiling condensation products. This liquid passes a separator (2), then a let-down valve (3) for pressure release, and enters a flash evaporator (4) where the major part of inerts and unconverted reactants is taken overhead. The flashed off gases are compressed and returned to the reactor. The liquid from the flash evaporator is heated and passes to a distillation column (5), from which vaporized aldehydes are taken as head stream. The bottoms

pass a second distillation column (6) with subatmospheric pressure in order to concentrate the catalyst solution. The gaseous aldehydes taken from two distillation columns are condensed and purified (7) [36]

BASF Process The BASF process also makes use of a gas recycle to separate aldehyde and catalyst solution. The process scheme corresponds to the gas recycle process that is shown in Figure 9.
The following reaction conditions are stated to be typical: temperature 110 $°C$, pressure 15-17 bar, Rh concentration < 200 ppm, TPP concentration 3-5 wt.%, and H_2/CO 55:45 [37].

Mitsubishi Process Mitsubishi uses several feature of common technology and operates an LPO process as a combination of gas and liquid recycle. The reaction temperature and the pressure are 100 $°C$ and 15-18 bar, respectively. The concentration of rhodium is about 300-350 ppm with about 20-22 wt.% TPP concentration. The synthesis gas is fed with H_2/CO ratio of 1.015:1 [38].

Ruhrchemie/Rhône-Poulenc (RCH/RP) Process RCH/RP process is based on a water soluble rhodium catalyst, namely $HRh(CO)(TPPTS)_3$ complex. The use of a water soluble catalyst system brings substantial advantages for industrial practice, because the catalyst can be considered to be heterogeneous. The separation of catalyst solution and reaction products, including high-boiling by-products, is achieved most simply and efficiently.
Losses of the rhodium in the crude aldehyde stream are negligible. High-boiling by-products do not dissolve in the aqueous catalyst, dispending with the need for continuous catalyst regeneration. Purification of synthesis gas and propene is not necessary, because the catalyst is not sensitive to oxo poisons that may enter with the feed.
Figure 11 shows the flow sheet of RCH/RP process. The unit is essentially a continuously stirred tank reactor, followed by a phase separator and strip column. The reaction takes place in the reactor (1) which contains the catalyst solution and the

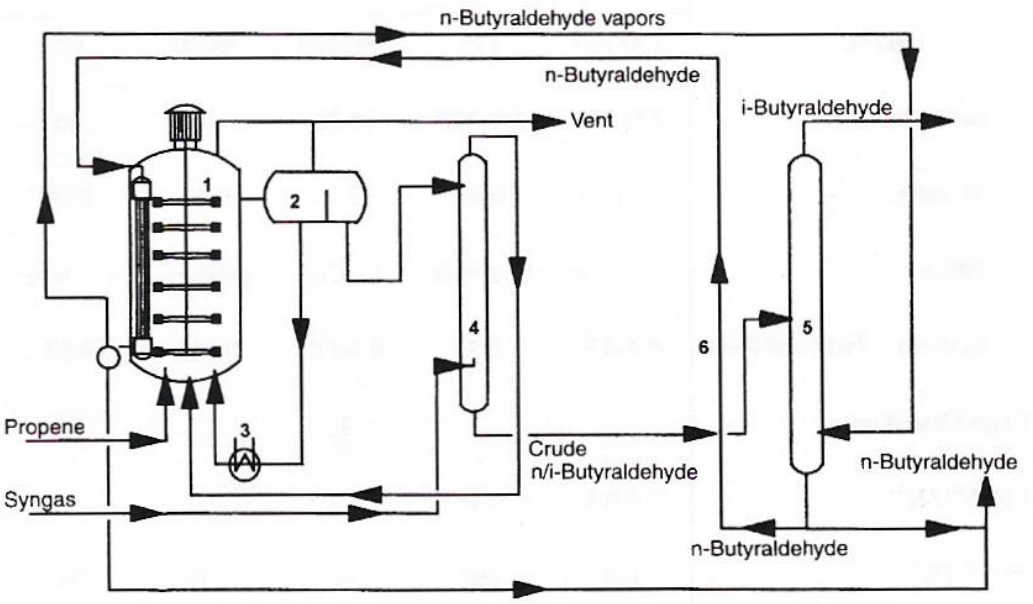

Figure 11: Flow diagram of Ruhrchemie/Rhône-Poulenc (RCH/RP) process.

reactor is fed with synthesis gas and propene. Before entering the reactor, the synthesis gas is first passed through a stripping column (4) in countercurrent to the crude aldehyde stream in order to recover the unreacted propene. The crude aldehyde product leaves the top of the reactor and passes into the decanter (2) where it is degassed and separated from the entrained catalyst solution. The catalyst solution is returned to the reactor via heat exchanger (3). The organic phase, containing the raw aldehyde, then passes through stripping column (4). Then the raw aldehyde is distilled into n- and iso-butanal (5). The heat of the reaction is used in a falling film evaporator (6) that has a function as reboiler of this distillation column.

2.1.5 Influence of Process Parameters

Effect of temperature is almost same for all type of catalysts (unmodified and modified cobalt and rhodium). The rate of the oxo synthesis increases with higher temperatures. The n/b ratio decreases for almost all olefins toward higher temperatures. The decrease of the n/b ratio is more pronounced with modified rhodium catalysts. This tendency is inverse for α-olefins bearing a functional group which is directing the regioselectivity toward linear products.

Raising the hydrogen partial pressure increases the reaction velocity and to some extent the n/b ratio. However, hydrogen partial pressure has no considerable effect on the n/b ratio at high p(H_2) ($> 60\ bar$). Increasing the carbon monoxide partial pressure has negative effect on the reaction rate at high p(CO) whereas positive effect at low p(CO) [39]. These are true for both unmodified and modified catalysts. Following equilibrium is formulated for ligand modified catalyst:

$$\mathrm{HM(CO)}_x + y\ \mathrm{PR}_3 \rightleftharpoons \mathrm{HM(CO)}_{x-y}(\mathrm{PR}_3)_y + y\mathrm{CO}$$

The equilibrium shifts to the right handside at low p(CO) and formation of linear aldehyde is favored. The n/b ratio decreases with increasing p(CO). At higher partial pressures the species $HM(CO)_4$ becomes dominant, thus favoring the linear product again [40].

The increasing ligand/metal ratio increases the n/b ratio in general whereas the catalytic activity varies in a nonlinear fashion as a function of phosphine concentration (Figure 12). Reactivity reaches a maximum at a point where the selectivity of the reaction remains constant.

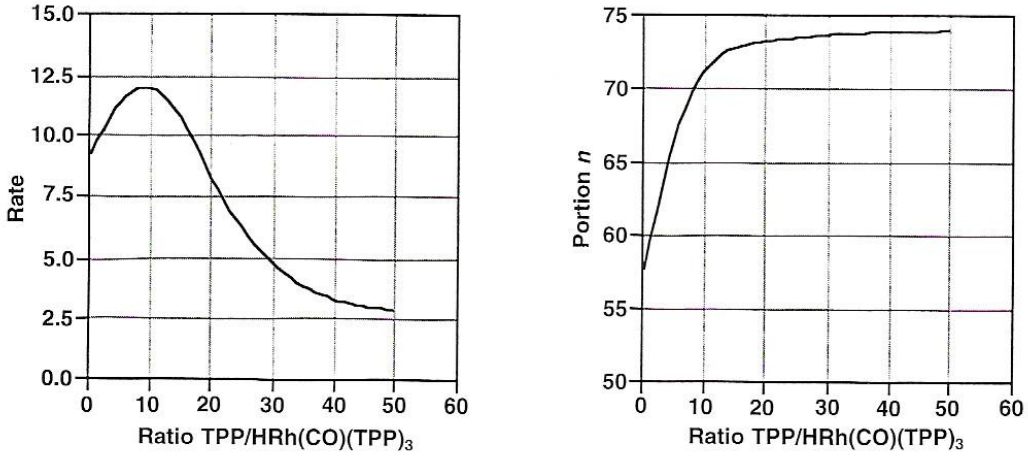

Figure 12: Effect of phosphine/rhodium ratio on reaction rate and selectivity [3].

2.2 Microemulsions

When water is mixed with an organic liquid and amphiphile, a turbid milky emulsion is obtained. Emulsion is a heterogeneous system of one immiscible liquid dispersed in another in the form of droplets. The droplet size for ordinary emulsion (macroemulsions) is more than 1 μm [41]. Emulsion has thermodynamic instability, thus after some time separates again into an aqueous and an organic phase.

In 1950s Shulman observed that these unstable water oil dispersions can be converted into optically transparent and thermodynamically stable mixtures by adding alcohol [42]. These mixtures were called microemulsion. A microemulsion is a thermodynamically stable dispersion of one liquid phase into another, stabilized by an interfacial film of surfactant. This dispersion may be either oil-in-water (o/w) or water-in-oil (w/o). The size of the droplet ranges from 4 to 100 nanometers, hence the microemulsion solutions are apparently transparent. The droplet can have structures such as spheres, rods or disks, depending on the composition and types of surfactant and oil used. The interfacial tension between the two phases is extremely low.

The microemulsions are characterized by the weight fraction of surfactant, γ, in the ternary mixture, the weight fraction of oil, α, in the mixture of oil and water and the molar ratio of water to surfactant w_0 [43].

$$\gamma = \frac{m_{surfactant}}{m_{surfactant} + m_{water} + m_{oil}} \tag{4}$$

$$\alpha = \frac{m_{oil}}{m_{water} + m_{oil}} \tag{5}$$

$$w_0 = \frac{n_{water}}{n_{surfactant}} \tag{6}$$

Reverse micelles are formed by association of polar head groups of amphiphiles with

colloidal drops of water in an organic medium in such a way that the polar head groups are directed into the water domains and the hydrocarbon tails are pointed into the hydrocarbon regions. The diameter of the reverse micelles is proportional to the value of w_0. g is a specific factor for every system, given in Angstroms.

$$d_{micelle} = g * w_0 \quad and \quad g = 1\mathring{A} \quad for\ alkylpolyglycolethers \tag{7}$$

Because of the presence of three entirely different polarity domains: polar aqueous, nonpolar organic, and interfacial regions, the microemulsion have been found to be very useful as reaction, extraction, and separation media. The aqueous core of microemulsion contributes to the solubilization of water-soluble compounds in nonpolar organic phase whereas the organic bulk phase offers the advantages of dissolving organic solutes. It is noted that the size of the aqueous core can be easily tuned by varying the water content of the microemulsion to host a variety of solutes ranging from dye to large protein molecules [44]. From the reaction point of view, microemulsions find several application fields such as nanoparticle preparation, polymerization, organic synthesis. On the basis of microemulsions Menger and co-workers [45] developed a methods for an economical environmental cleanup of chemical warfare contamination. As an example of organometallic catalysis in a microemulsion, Beletskaya [46] performed palladium catalyzed C-C coupling reactions in aqueous medium with a very high content of surfactant.

The study of phase behavior of the ternary mixture is a matter of common scientific and technological interest from both theoretical and experimental point of view because types (either water or oil continuous type), stability, phase inversion, and preparation method of ordinary ternary mixture are related to the phase behavior in surfactant system.

The following sections cover the phase behavior and general information about surfactants.

2.2.1 Surfactants

Surfactants, also known as wetting agents, is a molecule that, when added to a liquid at low concentration, changes the properties of that liquid at a surface or interface and lower the surface tension of a liquid, allowing easier spreading. The term surfactant is a compression of "Surface active agent". Surfactants are usually organic compounds that contain both hydrophobic and hydrophilic groups, and are thus semi-soluble in both organic and aqueous solvents. Surfactants are also known as amphipathic compounds, meaning that they would prefer to be in neither phase (water or organic). For this reason they locate at the phase boundary between the organic and water phase, or, if there is no more room there, they will congregate together and form micelles.

The hydrophilic end is water-soluble and is usually a polar or ionic group. The hydrophobic end is water-insoluble and is usually a long fatty or hydrocarbon chain. This dual functionality, hydrophobic and hydrophilic, provides the basis for characteristics useful in cleaner and detergent formulations, including surface tension modification, emulsification, foam, and cloud point. Surfactants are generally characterized by the hydrophilic group into the following categories : anionic, cationic, nonionic and amphoteric.

Technical grade Marlipals (branched alcohol (poly) ethylene glycol ethers) are nonionic type surfactants with the structure R-O-(CH_2-CH_2-O)$_m$-CH_2-CH_2-OH. They are derived from alcohols via ethoxylation. There is neither a negative nor a positive charge in either part of the molecule, thus giving it the nonionic terminology. They are oil or water soluble depending on degree of ethoxylation.

2.2.2 Phase Behavior in a Surfactant System

Consider a ternary mixture of water, a hydrocarbon and a nonionic surfactant. Phase behavior of the ternary system as a function of field variable can be described by a Gibbs prism with oil-water-surfactant triangle as its base and the field variable as the ordinate [47]. At constant pressure the ternary system is specified by setting three independent variables. These are generally the temperature T, the weight

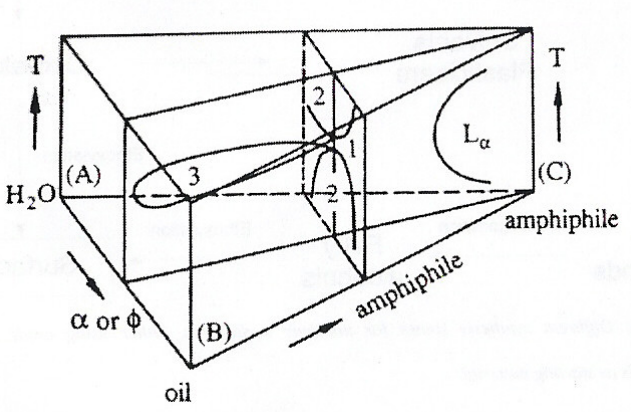

Figure 13: Schematic phase prism of a ternary mixture of water, oil and surfactant.

fraction of oil α, and the weight fraction of surfactant γ. Figure 13 represents the Gibbs prism with T as the ordinate.

In the ternary nonionic microemulsion system common phase sequence as a function of temperature is given as Type I → Type III → Type II [48] [49]. Today the common notation is $\underline{2} \rightarrow 3 \rightarrow \bar{2}$. The notation describes the change in the surfactant solubility from more water soluble (o/w, $\underline{2}$, Winsor type I) to more oil soluble (w/o, $\bar{2}$, Winsor type II). The progress of the phases can be illustrated on isothermal sections of the phase prism (cf. Figure 14).

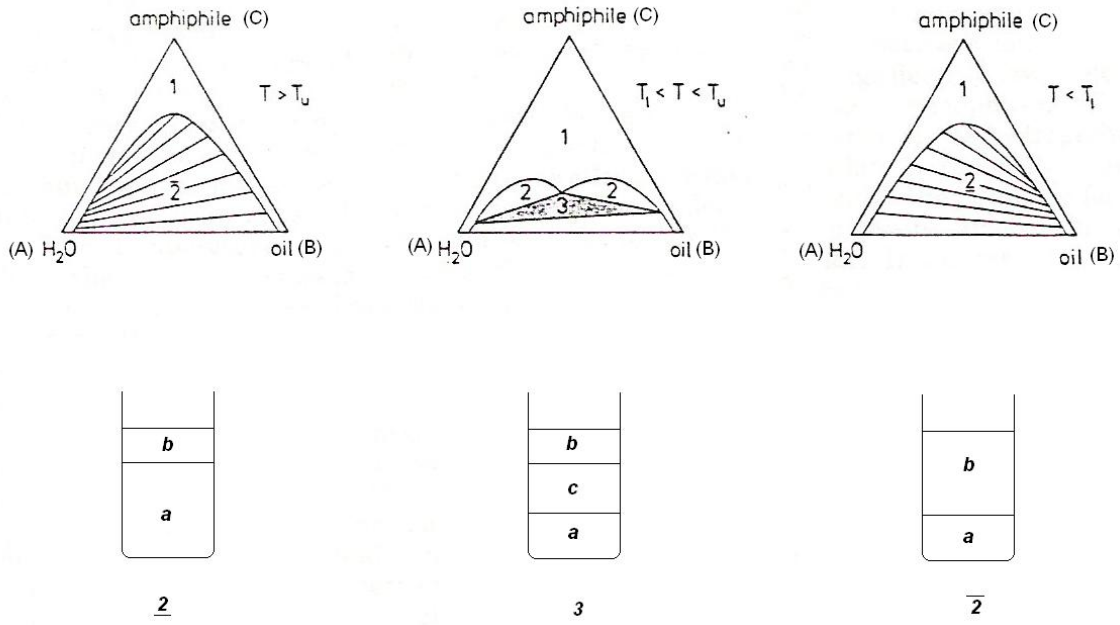

Figure 14: Isothermal sections of the phase prism.

When the surfactant is more hydrophilic at low temperatures, the surfactant dissolves mainly in water and forms oil-in-water (o/w) type microemulsion that is in equilibrium with an excess oil phase ($\underline{2}$). On the other hand, when the surfactant is more lipophilic at high temperatures, the surfactant dissolves mainly in oil phase and forms water-in-oil (w/o) type microemulsion in equilibrium with an excess water phase ($\bar{2}$). At intermediate temperatures, the surfactant separates from both water and oil and forms a bicontinuous type microemulsion phase that is equilibrated with excess water and oil phases (3).

In surfactant systems, temperature is a tuning parameter of this kind of phase transition and the temperature at which an o/w type microemulsion inverts to a w/o type microemulsion is called phase inversion temperature (PIT). On the other hand the formation of the microemulsion or aggregation of reverse micelle is depending on the surfactant concentration known as critical micelle concentration (cμc).

The shape of the phase diagram obtained at equal amounts of water and oil (α = 0.5) is that of a fish. The extent of the fish and the temperature at which it is located provides key information about the particular system of water, oil and surfactant [50]. Figure 15 shows the fish shape phase diagram (see also in Figure 13 ,the vertical section at $\alpha = 0.5$). At low surfactant concentrations, the phase sequ-

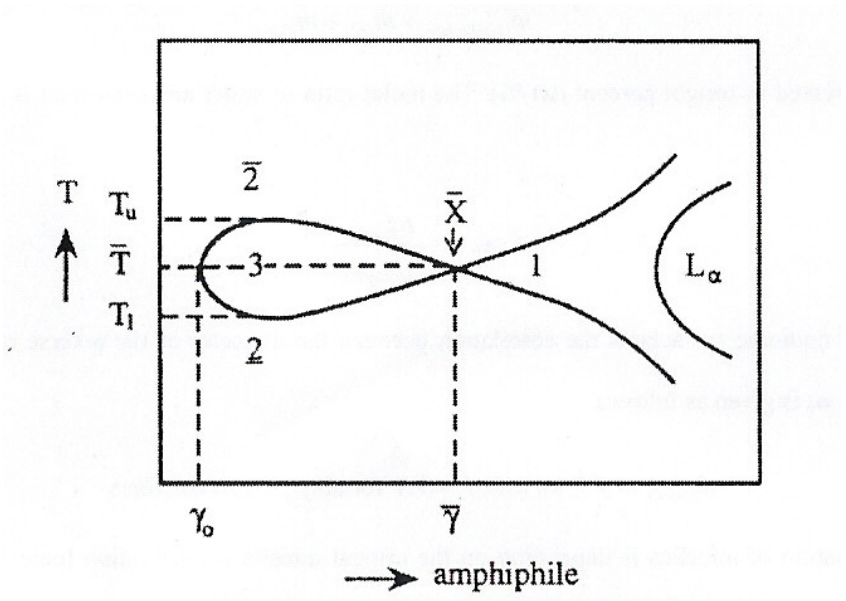

Figure 15: Section of the Gibbs prism at equal amounts of oil and water.

ence is $\underline{2} \rightarrow 3 \rightarrow \bar{2}$ as a function of temperature. Increasing the amount of surfactant result in the formation of single phase microemulsion surrounded by two two-phase regions. Finally, at higher surfactant concentrations a single homogeneous microemulsion phase is observed.

The surfactant concentration $\bar{\gamma}$ represents a measure of efficiency of the surfactant. That is the amount of surfactant required to completely solubilize equal amounts of water and oil. The temperature $\bar{T}$ is the phase inversion temperature.

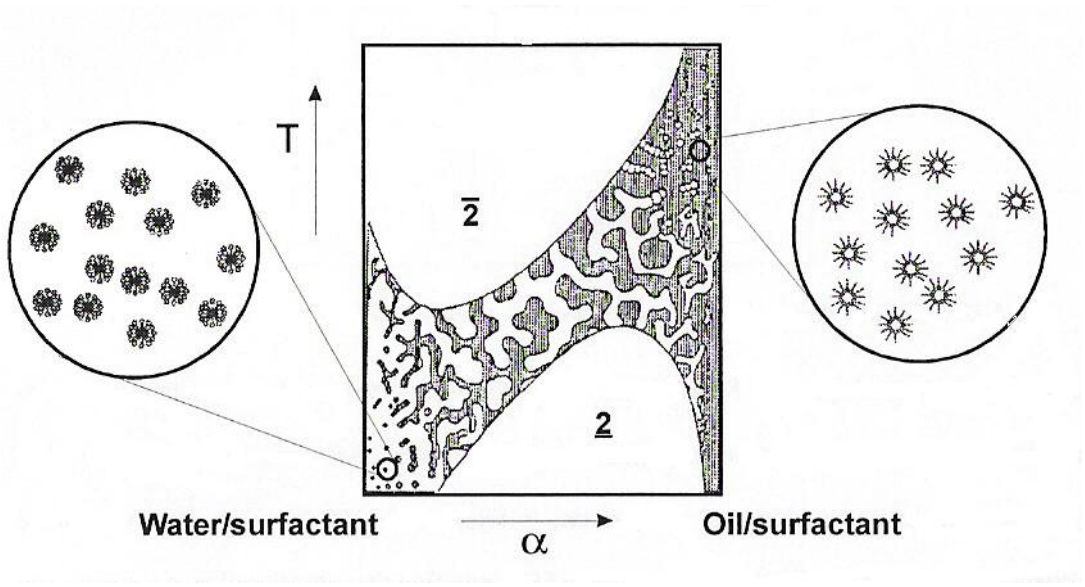

Figure 16: Section of the phase prism at constant surfactant concentration.

Another characteristic section of the Gibbs prism is a vertical plane at constant surfactant concentration (for a value of γ higher than $\bar{\gamma}$) (cf. Figure 16). This plane is perpendicular to the plane on which the fish are seen (see Figure 13). A region of isotropic single phase solution is observed extending from water-rich to oil-rich side of the phase prism and this single phase region is surrounded by two two-phase regions. On the oil-rich side, the mixtures consist of stable dispersions of water droplets in oil (w/o microemulsion) and the reverse micelles are formed. On the water-rich side, the mixtures consist of stable dispersion of oil droplets in water (o/w microemulsion) and the micelles are observed.

3 Experimental

3.1 Experimental Set-up

The reactions were performed in a stainless steel autoclave (Premex, Switzerland) which is directly mounted to an oil bath equipped with a temperature controller unit (Huber CC3, Germany). The autoclave was equipped with a gas dispersion stirrer and flow spoiler. The reactor was separated by a pressure regulator from a syngas vessel and that was separated from a syngas reservoir by a valve (cf. Figure 17 and 18). All hydroformylation reactions were performed according to following

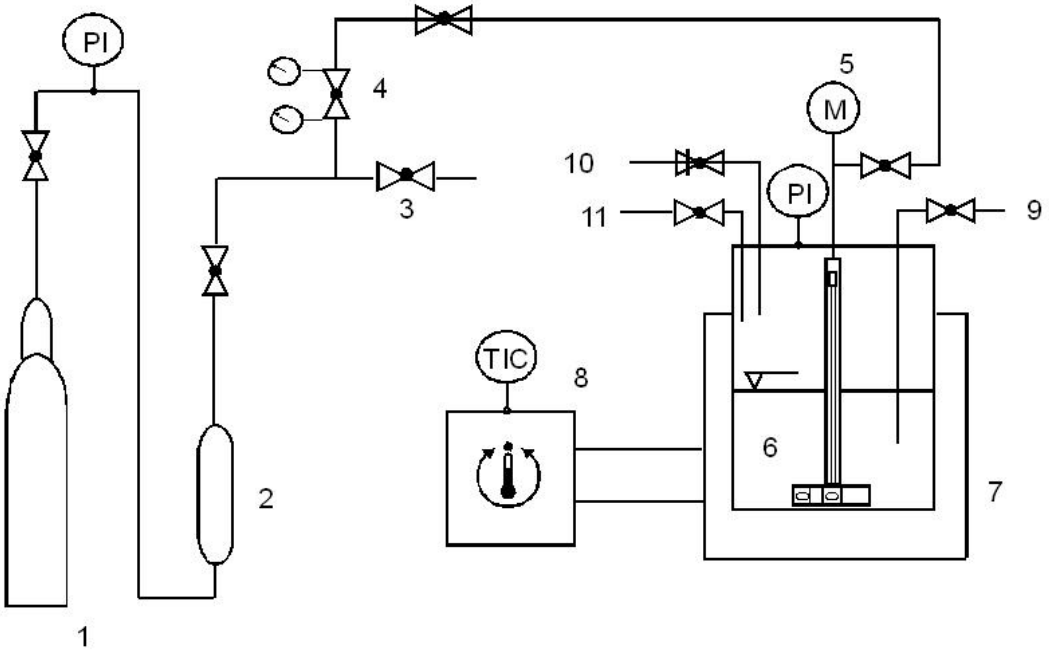

Figure 17: Layout of experimental set-up (1) gas reservoir in a security cell, (2) 300 *ml* gas vessel in a security cell, (3) pressure release valve, (4) pressure adjustment valve, (5) gas dispersion stirrer with flow spoiler, (6) 100 *ml* autoclave, (7) oil bath with (8) temperature control, (9) sampling valve, (10) 200 *bar* security valve, (11) pressure release valve.

procedure. The reaction mixture was added to the autoclave and the assembled autoclave was flushed three times with syngas and heated to a desired temperature. The stirring was started and then the autoclave was pressurized.

During the reaction syngas was supplied from the vessel and the pressure inside the reactor was kept constant by using the pressure regulator. Progress of the reaction

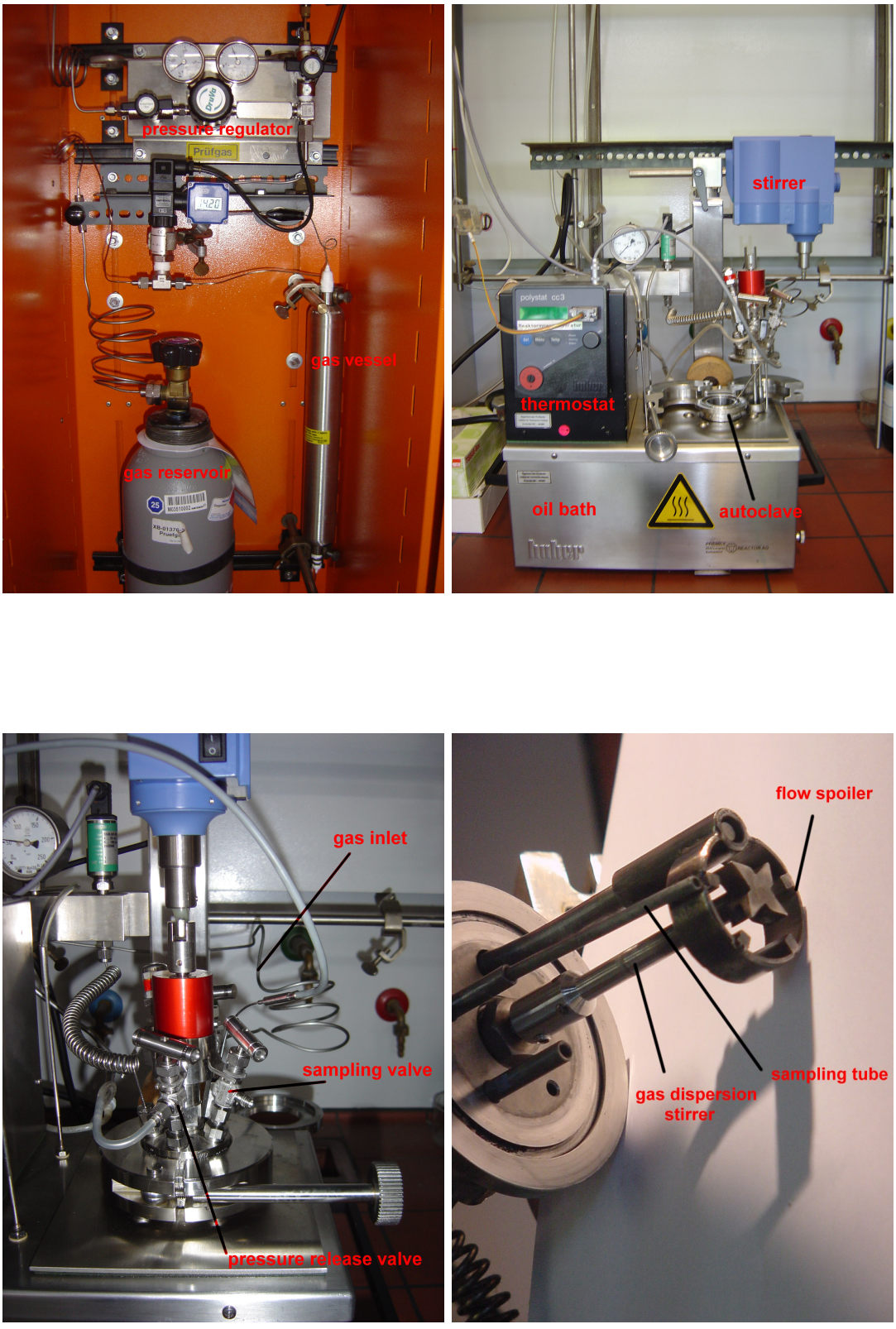

Figure 18: Photographs of experimental set-up.

was monitored by the pressure drop in the syngas vessel.

Samples were taken at intervals and analyzed by gas chromatography.

3.2 Analytical Methods

3.2.1 Gas Chromatography

The reaction products were determined by GC Sichromat 3 using Rtx-5MS capillary column and flame ionization detector. The length and inner diameter of the column and the film thickness was 50 m, 0.25 mm and 0.25 μm, respectively. Nitrogen was used as a carrier gas. For the separation of the organic products a heating program was applied. The initial temperature of the column was adjusted to 80 $°C$ and kept constant for 2 min, then the column was heated with a rate of 20 $°C/min$ until 280 $°C$ was reached and kept again constant at this temperature for 5 min. The recorded signal was analyzed and integrated by HP ChemStation software. Products were identified by comparison of the retention times and spectral characteristics with authentic samples. The Figure 19 shows an example for the GC signal.

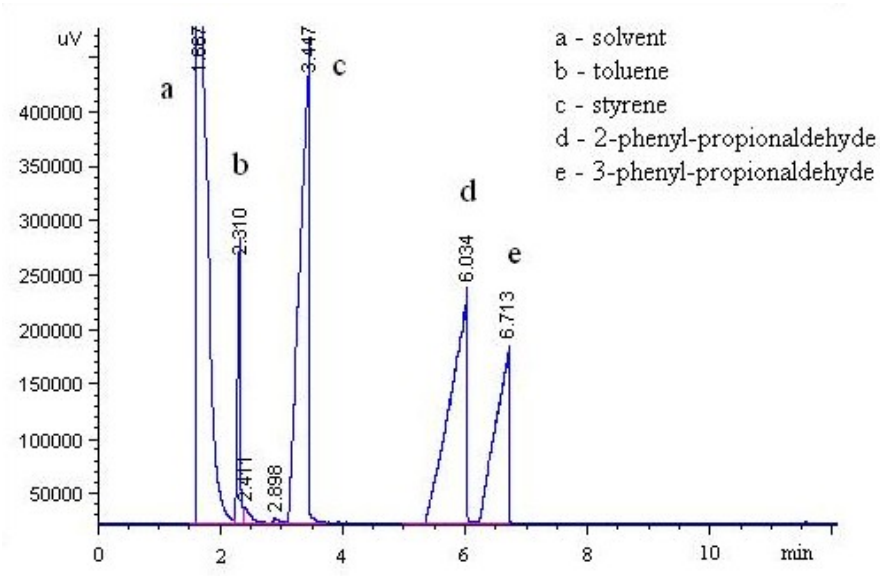

Figure 19: GC signal for hydroformylation of styrene.

3.2.2 Atomic Absorption Spectroscopy

Rhodium concentrations in the organic phase were determined after phase separation. Analysis was carried out by Perkin Elmer 2380 spectrometer. The measurement conditions were as follow. 343.5 nm wavelength, 0.2 nm gap, 0.4 air/acetylene ratio.

3.2.3 Infra-red Spectroscopy

Formation of the various rhodium carbonyl complexes during hydroformylation in microemulsion was studied in-situ by means of high-pressure infra-red (HP-IR) spectroscopy. Details of these measurements are given in Section 7.2.

4 Rhodium Catalyzed Hydroformylation of 1-Octene in Microemulsion: Comparison With Various Catalytic Systems

4.1 Introduction

Hydroformylation of olefins is an important, well-known commercial process for the production of aldehydes and alcohols, moreover it is one of the most important applications of homogeneous catalysis in industry as well [3].

The history of aqueous, biphasic homogeneous catalysis starts with the initial observation by Manassen [51]. Since the first industrial use of this system in 1984 by the hydroformylation of propylene in the plants of Ruhrchemie A.G, research into aqueous, two phase, homogeneous catalysis has become very active [52] [53]. Two basic problems in classical homogeneous catalysis, namely the separation and subsequent recycling of the catalyst can be elegantly solved by using two phase catalysis in which the catalyst and the product enables to be separated by simple phase separation [9]. However, if we compare biphasic reactions with their monophasic equivalents, it is found that the rates are lower in the two phase systems [54]. Although the use of water as a second phase has many advantageous [53], it has also its limitations, especially when the water solubility of starting materials is too low, preventing adequate transfer of the organic substrate into aqueous phase or at the phase boundary and consequently reducing the reaction rates [55]. Therefore, this process is not economically viable for long chain alkenes, which are not very soluble in water.

One useful way to overcome this solubility problem that is frequently encountered in organic reactions is performing the reaction in a microemulsion [56] [57]. A microemulsion is formed by adding a suitable surfactant to biphasic system. The amphiphilic nature of this substance lowers the interfacial tension of water and oil and accelerates the rate of the reaction because aggregates such as micelles or microemulsion droplets form [58] [50].

This strategy has been used in the hydroformylation of long chain alkenes [59]

[60]. The cationic surfactants such as cetyltrimethylammoniumbromide (CTAB) were used in the hydroformylation of various alkenes with $Rh - TPPTS$ system [61]. High activity and selectivity was observed in the hydroformylation of 1-octene and 1-decene using rhodium complex associated with sulfonated diphosphines in the presence of ionic surfactants or methanol [62].

Understanding of the reaction mechanism and the characterization of the intermediates present during the reaction are important aspects of studies of the rhodium catalyzed hydroformylation [63] [64].

The reaction kinetics and the resting state of unmodified rhodium carbonyl catalyst have been extensively studied [65] [66]. The active species is generally assumed to be $HRh(CO)_3$, which is formed by dissociation of a CO ligand from the $HRh(CO)_4$ complex.

The hydroformylation mechanism for phosphine modified rhodium catalysts and the coordination chemistry of several rhodium phosphine complexes that are potential intermediates in the reaction were studied by Wilkinson and co workers [67] [68]. It appeared that the principal active catalytic species was $HRh(CO)_2(PPh_3)_2$ under the conditions studied [69]. The active species are generated by preliminary equilibrium (Figure 20). Depending on the reaction conditions, the predominant catalyst species are coordinated by one or more phosphine ligands.

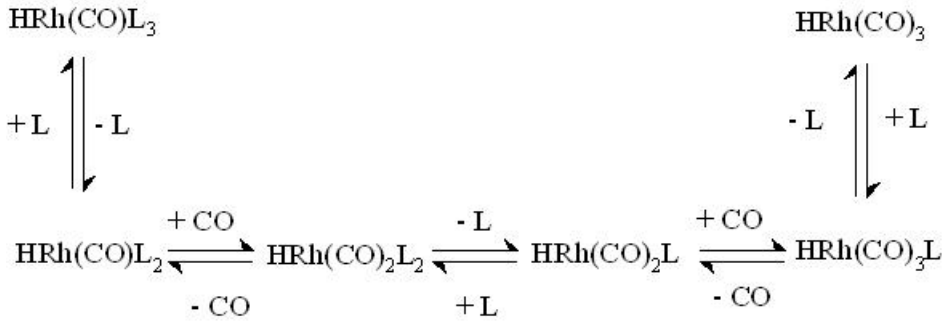

Figure 20: Equilibria between the active species. L= TPP, $TPPTS$.

Previously, it was reported that the use of nonionic surfactants of alkylpolyglycolether results in high reaction rates in the hydroformylation of 1-dodecene [70]. It was also recently studied hydroformylation of 7-tetradecene in a microemulsion [71].

At temperatures around 120 $°C$ and under pressure of 100 bar 7-tetradecene is hydroformylated with high regioselectivity. Under the reaction conditions studied, the equilibria between various catalytically active complexes is shifted towards the unmodified rhodium carbonyl $HRh(CO)_3$.

As a continuation of our investigation on microemulsion systems in hydroformylation reaction, we here described how addition of nonionic surfactant affects the hydroformylation of 1-octene by rhodium complex with triphenylphosphine sulfonate ($TPPTS$). The combination of the experiments under comparable homogeneous and biphasic conditions were performed in order to make direct comparison of microemulsion with classical systems. In addition, the influence of the ligand excess and the amount of the surfactant on the reaction rate and selectivity were discussed.

4.2 Experimental

4.2.1 General Methods

All chemicals were purchased from Fluka or Sigma-Aldrich and used as received unless otherwise indicated. The technical grade surfactant Marlipal $O13/E_i$ (alkylpolyglycolether derived via ethoxylation of isodecanol), syngas (CO/H_2 1:1) were purchased from Condea Chemicals and Messer Griesheim, respectively. The ligand used was 30.7 $wt.$ % aqueous solution of $TPPTS$ from Celanese.

The hydroformylation reactions were performed in 100 ml stainless steel autoclave (Premex) equipped with temperature controller (Huber CC3) and mechanical stirrer. The pressure inside the reactor was kept constant throughout the whole reaction time by using a gas reservoir along with a pressure regulator. Progress of the reaction was monitored by the pressure drop in the syngas reservoir. The reaction products were analyzed by gas chromatography (Sichromat 3) using Rtx-5MS capillary column and FID. The experiments were reproduced in order to gain confidence.

4.2.2 Standard Hydroformylation Reaction

Standart experiments were carried out at temperature 85 $°C$ and syngas pressure of 60 bar (CO/H_2 1:1). The rhodium concentration of the reaction mixtures was

200 *ppm* with respect to substrate in all experiments. Preparation of the reaction mixtures was carried out as follows:

Microemulsion: The catalyst precursor rhodium dicarbonly acetylacetonate $Rh(acac)(CO)_2$ (0.05 *mmol*) and a proper amount of water soluble ligand tris-(3-sulfophenyl)-phosphine trisodium salt ($TPPTS$) in 2.5 *ml* degassed water were stirred under nitrogen atmosphere for 24 *hr*. The resulting catalyst solution was added to 24.7 *gr* olefin and 3.9 *gr* nonionic surfactant to give the microemulsion. Composition of the microemulsions was 79 *wt.*% of alkene, 13 *wt.*% of surfactant and 8 *wt.*% of aqueous catalyst solution.

Biphasic: Composition and preparation procedure of the catalyst solution was the same with the solution that was prepared for the microemulsion. This solution was added to the olefin phase.

Biphasic associated with co solvent: The catalyst solution was prepared as in microemulsion and the resulting solution was added to a proper amount of olefin in 30 *ml* toluene.

Homogeneous: The rhodium precursor $Rh(acac)(CO)_2$ (0.05 *mmol*) and proper amount of triphenylphospine (TPP) were dissolved in 2.5 *ml* toluene and added to the olefin.

Unmodified: The rhodium precursor $Rh(acac)(CO)_2$ (0.05 *mmol*) was dissolved in 2.5 *ml* toluene and added to the olefin.

4.3 Results and Discussion

One of the purposes for developing microemulsions was to generate a catalysis system capable of transforming long chain alkenes. For this purpose, 1-octene was chosen to test the concept of microemulsion catalysis.

The product identification and the material balance were examined under microemulsion condition with ligand/metal ratio 10. Major byproducts formed were internal

alkenes 2-octene and 3-octene due to isomerization of the substrate.

The typical course of the reaction at standard conditions is shown in Figure 21. As can be easily seen from the figure, the octene conversion increases linearly with the reaction time up to 80 % of the total conversion. The linear aldehyde selectivity (n/b) is constant during that time and the amount of the isomerization products reach a maximum value of 37 %. The internal octenes formed via isomerization are hydroformylated when the reaction of 1-octene begins to slow down. The internal double bond is converted into the branched aldehydes. Therefore, hydroformylation of the isomerization products causes a decrease of the initial linear to branched aldehyde ratio. Because of this concentration-time profile of the reaction, linear aldehyde selectivities of a catalyst should be observed before the disturbance by isomerization products in order to make consistent discussion. This is probably the reason why some authors observed low linear aldehyde selectivities with high reaction rates and vice versa [72].

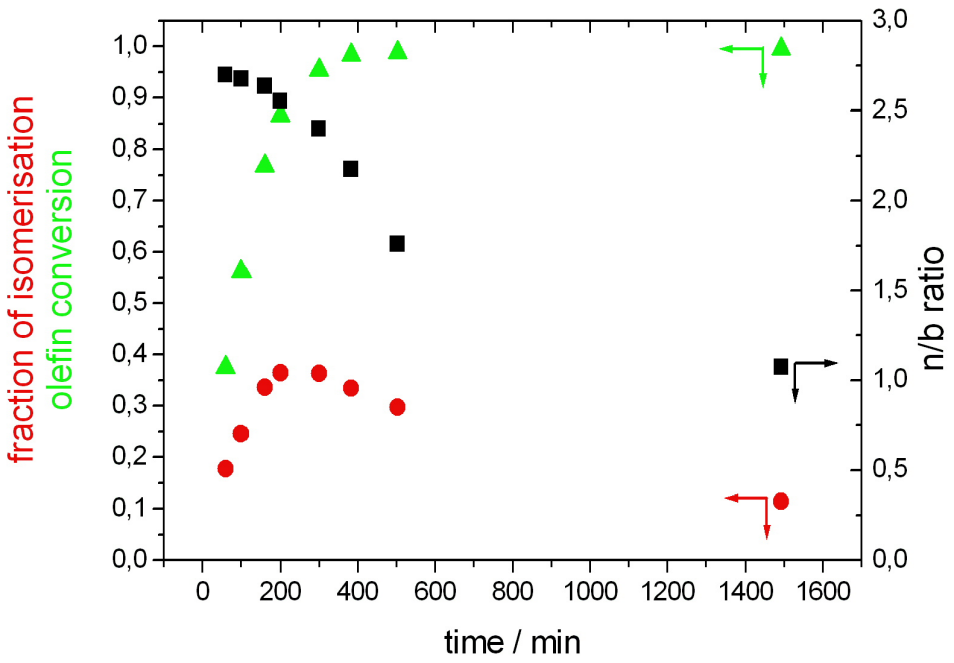

Figure 21: Typical course of the hydroformylation reaction of 1-octene. 85 $°C$, 60 *bar*, 200 *ppm* Rh, Ligand/Metal=10.

The possible sources of the branched aldehyde formation include alkene isomerization, regioselectivity of the addition of the metal carbonyl to the alkene and isomerization of the alkyl and acyl species. Lazzaroni [73] [74] studied the relation between the observed isomerization and the linear to branched ratio and showed that isomerization is a result of β-hydride elimination of the isoalkyl bonded to the rhodium. The amount of the isomerization is expected to increase with higher temperatures and lower pressures because this reaction has higher free energy of activation than hydroformylation and requires vacant site. For hydroformylation of hex-1-ene, at a reaction temperature of 100 $^{\circ}C$, for linear alkyl, the hydroformylation predominates β-hydride elimination, for branched alkyl, elimination predominates hydroformylation.

Because only the isoalkyl rhodium forms internal alkenes, the amount of the branched aldehyde diminishes during the isomerization in the present system. Since the internal alkenes are less reactive than the terminal alkenes, hydroformylation of isomerization products take place at high conversions and the regioselectivity depends on the conversion.

4.3.1 Variation of the Catalytic System

In order to make a comparison of our microemulsions with the other systems, experiments were also carried out using catalysts such as, unmodified rhodium $HRh(CO)_4$ and $HRh(CO)(PPh_3)_3$ in homogeneous system, water-soluble $Rh-TPPTS$ complex in two-phase system and in association with co-solvent.

First, all the reactions were performed with ligand/metal ratio of 4. A comparison of the performance of these catalysts is shown in Figure 22. Conversion to aldehyde, i.e. mol of aldehyde per mol of substrate transformed, is drawn against reaction time for each catalytic system. It indicates considerable high reaction rates in homogeneous systems (in both unmodified rhodium $HRh(CO)_4$ and $HRh(CO)(PPh_3)_3$), as expected.

The result of $Rh-TPPTS$ catalyst in water/toluene showed high activity with respect to biphasic equivalent. This is probably due to the increase in the solubility

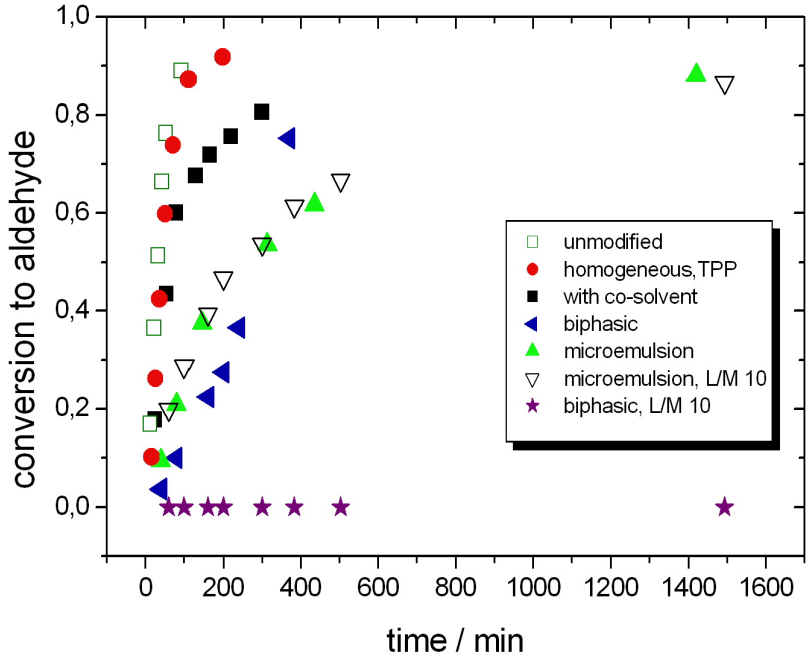

Figure 22: Hydroformylation of 1-octene with various catalytic system. 85 $°C$, 60 bar, 200 ppm Rh, Ligand/Metal=4.

of catalyst in the organic layer.

The catalytic activity that is observed in the biphasic system is higher than expected for this kind of poorly water-soluble organic reagent. This surprising result raised the question whether the active species is still the water-soluble $Rh - TPPTS$ complex or unmodified rhodium carbonyl complex ($HRh(CO)_3$) which is formed by loosing of the $TPPTS$ ligand as indicated in Figure 20. To answer this question, the experiments under microemulsion and biphasic conditions were repeated with higher ligand/metal ratio (L/M=10). Conversion to the aldehydes was only 0.3 % after 24 hr under biphasic condition. This observation indicates that the ligand/metal ratio of 4 is not sufficient to convert all the rhodium into the water-soluble complex. The organic-soluble rhodium carbonyl is dominantly present in two-phase system with this low ligand excess.

It seems that the water-soluble rhodium complex is the active species with both ligand/metal ratios under microemulsion condition, hence the concentration time

profile remained equal as the ligand/metal ratio was increased. Furthermore, the active species during the hydroformylation of 1-octene in microemulsion medium has been investigated using high pressure infrared spectroscopy(HP-IR) [75]. The results reveal that $HRh(CO)_2(L)_2$ is the resting state of the catalyst at the ligand/metal ratios greater than 2 under the microemulsion conditions studied.
The influence of the catalytic system on linear aldehyde selectivity and the amount of isomerization product are presented in Figure 23 and 24, respectively.

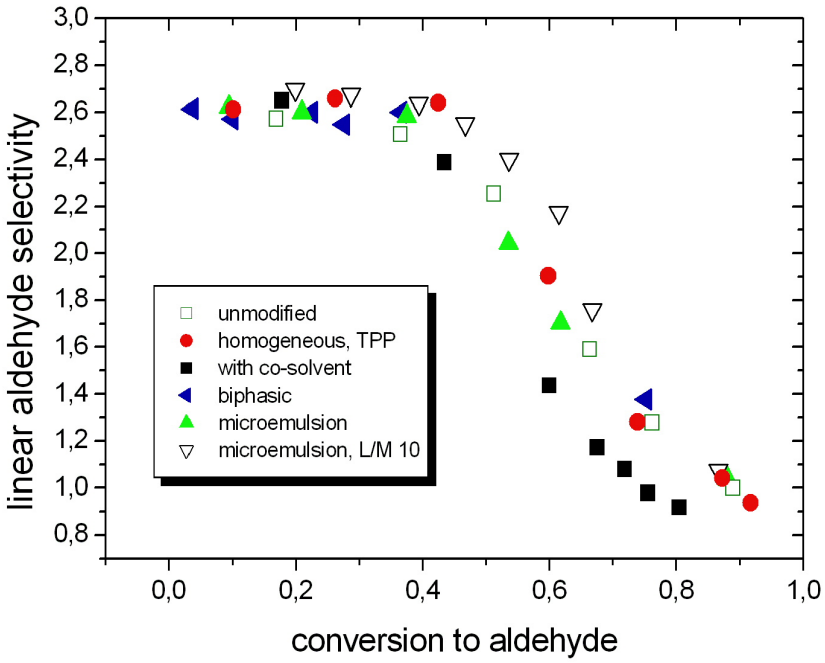

Figure 23: Effect of variation of the catalytic system on linear aldehyde selectivity. 85 $°C$, 60 bar, 200 ppm Rh, Ligand/Metal=4.

The disturbance in the initial selectivity is observable with all catalyst systems and the results correspond well with the typical reaction pattern under microemulsion conditions shown in the previous section. Surprisingly, no significant change in the initial linear aldehyde selectivity is observed as the catalytic systems have changed. Neither addition of the surfactant or the co-solvent to the two-phase system nor change of the catalyst from unmodified rhodium carbonyl to $Rh-TPP$ or $Rh-TPPTS$ complexes has any considerable influence on the selectivity.

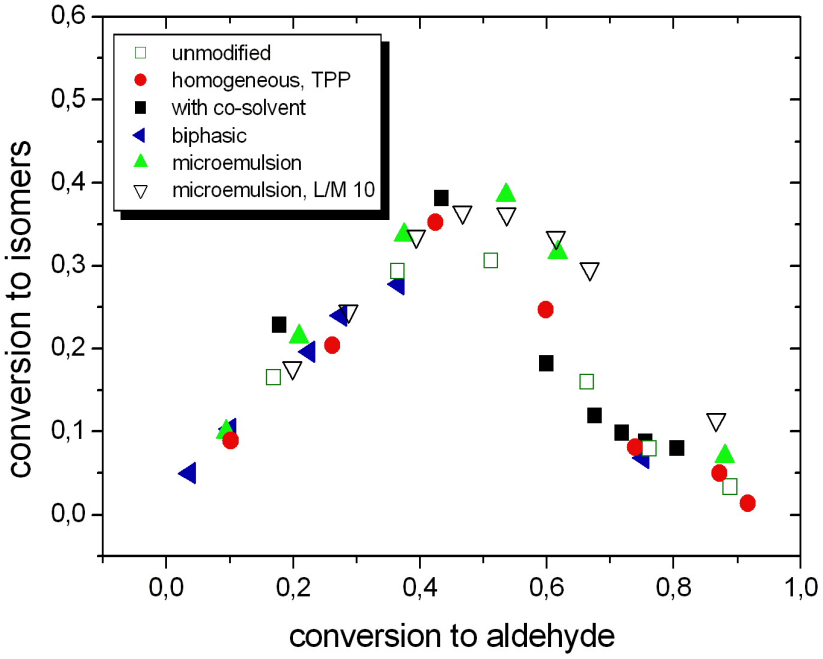

Figure 24: Effect of variation of the catalytic system on amount of isomerization product. 85 $°C$, 60 bar, 200 ppm Rh, Ligand/Metal=4.

The isomerization products increase with reaction time up to total olefin conversion of 80 % (50 % conversion to the aldehydes) and reach a maximum value. A change of the catalytic system has no remarkable effect on the ratio of rate hydroformylation to rate of isomerization.

4.3.2 Influence of the Ligand Excess

In order to gain better understanding of the behavior of the microemulsions, further investigations were carried out on the ligand excess. Thus, the ligand/metal ratio was varied between 4 and 40. The effect of the ligand excess on the initial reaction rate is illustrated in Figure 25.

Under biphasic conditions, the initial reaction rate at ligand/metal ratio of 4 is higher than expected for the poor water soluble substrate. As previously indicated, high initial reaction rate reveals that the equilibrium between various active species shifts towards unmodified rhodium carbonyl complex under biphasic condition at low ligand concentrations. At higher ligand concentration the rhodium species are

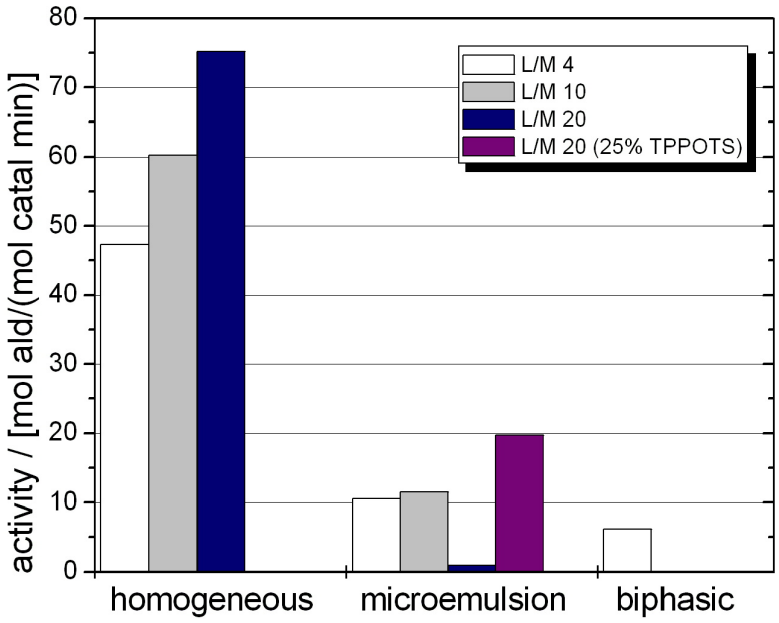

Figure 25: Influence of ligand excess on initial reaction rate. 85 $°C$, 60 bar, 200 ppm Rh.

modified by the ligand and no hydroformylation of the water-insoluble substrate is obtained.

The initial reaction rates are accelerated towards higher ligand excess under homogeneous ($HRh(CO)(PPh_3)_3$) condition. This effect was already described by Olivier et. al. [76]. The catalytic activity varies in nonlinear fashion as a function of phosphine concentration. The activity increases as the phosphine concentration increases and reaches a maximum, further increase in ligand concentration leads to lower rates. This is due to hindrance of the formation of the active species $HRh(CO)_2(L)_2$ at high ligand concentration.

Under microemulsion condition, the initial reaction rates remain constant as the ligand concentration increases from 4 to 10 and decreases with further ligand excesses. It is reasonable to state that even with low ligand concentrations, the active species are modified and the decreasing trend in the catalytic activity begins at lower ligand excess in compare to homogeneous equivalent. These effects are due to the high local ligand concentration inside the small reverse micelle.

To avoid any question on oxidized $TPPTS$ in our reaction conditions, we tested indirectly for the presence of oxidized $TPPTS$ by the catalytic activity. Thus, the reaction was performed at the ligand/metal ratio of 20 with 25 mol % oxidized $TPPTS$ under microemulsion conditions. The catalytic activity is even higher than the activity observed at lower ligand concentrations. The result suggests that oxidation of the ligand is not pronounced under the conditions studied.

Table 2: Variation of the ligand excess with various catalytic systems.

Catalytic System	Ligand	L/M[a]	n/b[b]
Homogeneous	TPP	4	2.66
		10	2.71
		20	2.93
Microemulsion	TPPTS	4	2.62
		10	2.70
		20	2.91
		40	*
	TPPTS+TPPOTS[c] (25 %)	20	2.61
Biphasic	TPPTS	4	2.61
		10	*

* no reaction.
a: ligand per metal ratio.
b: ratio of linear to branched aldehyde.
c: oxidized tppts.

The results depicted in Table 2 show the influence of the ligand excess on linear aldehyde selectivity. The selectivities were recorded at low conversions (< 30 %) before the disturbance by isomerization products. In general the linear products show a gradual increase with increasing ligand/metal ratio. Coordination of the ligands to the metal center enhances the steric bulkiness and linear products are favored. However, this effect is very weakly pronounced, thus the n/b ratio varies between 2.6 and 2.9 as the ligand/metal ratio increases from 4 to 20. Moreover, as mentioned previously, change of the reaction medium or the ligand has no influence on the selectivity. It can be concluded that the selectivity is mainly affected by the structure of the 1-octene.

Another remarkable result is that the amount of the isomerization is slightly sup-

pressed towards high ligand/metal ratios in homogeneous and microemulsion systems. Under such conditions the metal center presents a more sterically hindered environment to the alkene and the formation of linear alkyl and acyl species are favored. As only the branched alkyl rhodium species will form internal alkenes, the amount of the internal alkenes diminish.

With the ligand/metal ratio of 20 (cf. Figure 26), the internal octenes that are formed via isomerization are not hydroformylated as the 1-octene conversion begins to slow down, therefore the disturbance in the initial linear aldehyde selectivities is not observable. Because the formation of the active species $HRh(CO)_2(L)_2$ is hindered by high ligand excesses, hydroformylation of the internal alkenes that is much more difficult than 1-alkenes is not possible under these conditions. Decrease in the amount of internal alkenes may due to reformation of 1-octene.

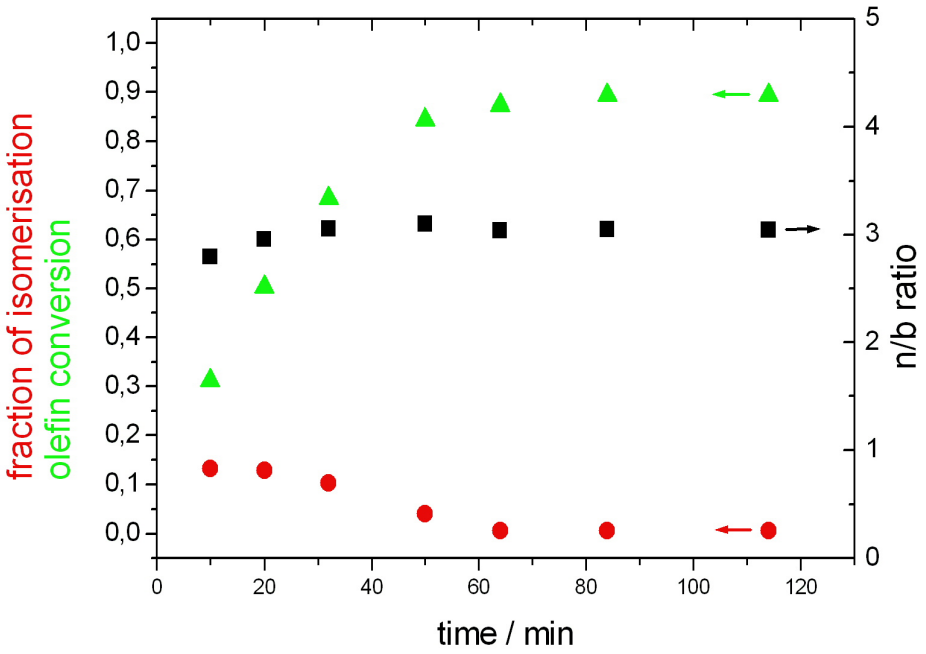

Figure 26: Course of the hydroformylation of 1-octene at high ligand concentration. 85 $^{\circ}C$, 60 *bar*, 200 *ppm* Rh, L/M=20, under homogeneous conditions.

4.3.3 Variation of the Surfactant Concentration

The influence of the surfactant concentration on the hydroformylation reaction was studied by varying the amount of the surfactant between 0 % and 3 %. Figure 27a shows the effect of surfactant on conversion. For more convenient discussion Figure 27b is plotted in following way: the linear aldehyde selectivities were recorded after 60 *min* reaction time (before the disturbance) in order to be sure about the consistency of the data and the conversions were recorded after 400 *min* in order to obtain a clear picture about the differences in rates (cf. Figure 27b).

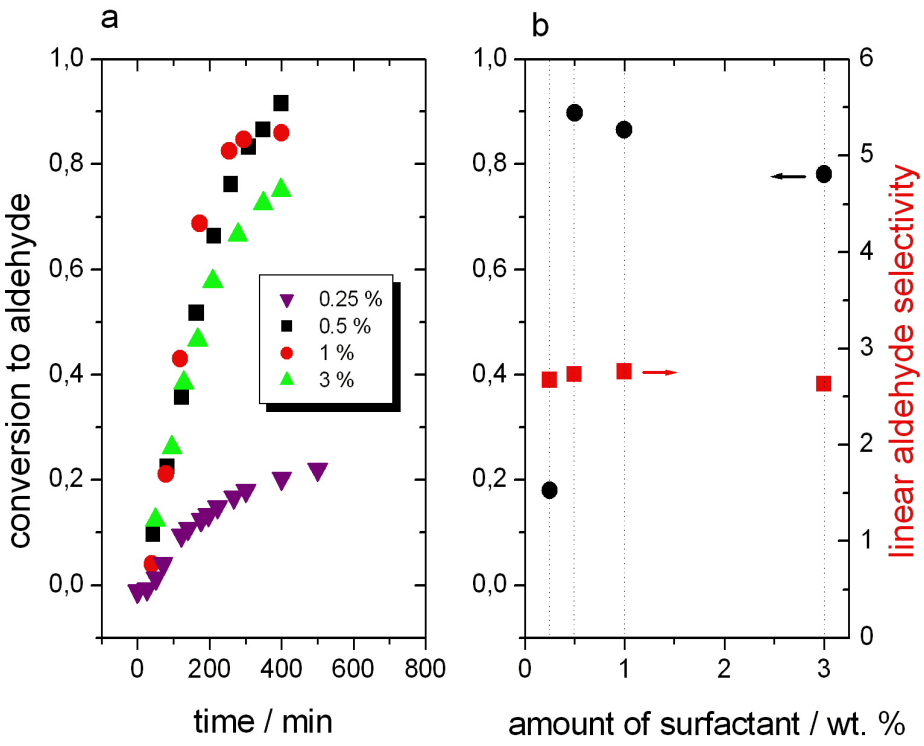

Figure 27: Effect of the surfactant concentration on conversion and linear aldehyde selectivity. 85 $^{\circ}C$, 60 *bar*, 200 *ppm* Rh, Ligand/Metal=10.

In the limit of no surfactant, no hydroformylation of the substrate is observed. Addition of small amount of the surfactant (0.5 wt.%) causes a considerable increase in the conversion. Further increase in the surfactant concentration leads to lower conversions again. This increase in the reaction rate can be explained by an increase in the interfacial area between organic and water phases when the surfactant is added to the system. The maximum of the reaction rate correlates with the critical

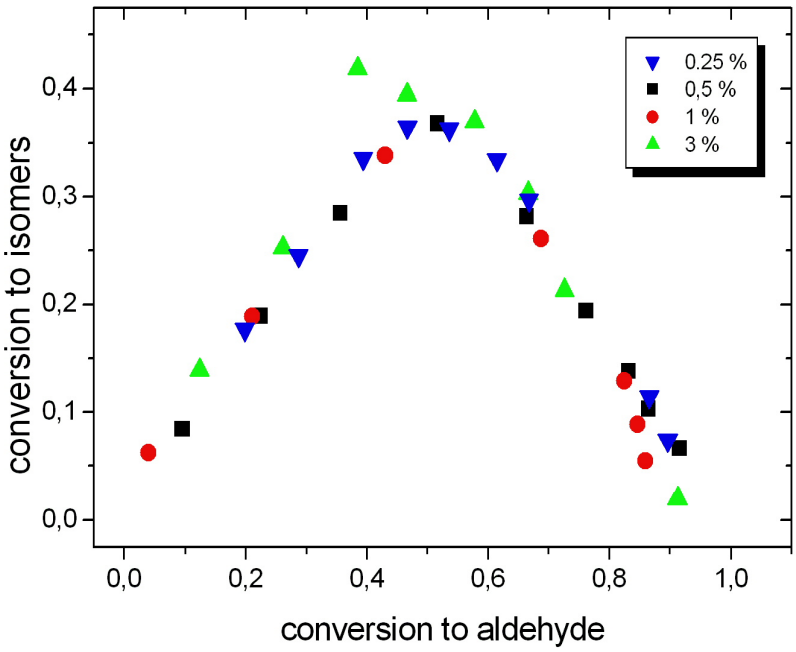

Figure 28: Effect of the surfactant concentration on amount of isomerization product. 85 $^{\circ}C$, 60 *bar*, 200 *ppm* Rh, Ligand/Metal=10.

microemulsion concentration (cμc) at which the reverse micelles are formed that act as host for the catalyst in the organic phase.

All the selectivities remain constant as the amount of the surfactant increases. We were not able to take any information from the selectivity values on any possible change in the active species by the addition of the surfactant, because even the change of the catalyst does not show any influence on the selectivity of 1-octene hydroformylation.

Figure 28 represents the effect of the surfactant concentration on the amount of the isomerization products and clearly indicates that there is no influence of the amount of surfactant.

4.4 Conclusions

Isomerization and hydroformylation of the 1-alkene are in competition during the reaction. When the hydroformylation of 1-alkene begins to slow down, hydroformyla-

tion of the isomerization products causes a disturbance in the initial linear aldehyde selectivity. This disturbance should be taken in consideration in order to ascribe all the observed effects to the varied conditions.
Following criteria show no considerable influence on the initial linear aldehyde selectivity for the hydroformylation of 1-octene;

1) change of the reaction medium from homogeneous to two-phase system, addition of the co-solvent or surfactant to two-phase system.
2) change of the catalyst from unmodified rhodium carbonyl to $Rh - TPP$ or Rh - $TPPTS$ complexes.
3) amount of the surfactant in microemulsion.

As all the reactions were hydroformylated with a moderate selectivity of about 2.65, the selectivities appeared to be more affected by the nature of the substrate.
Under biphasic conditions the equilibrium between various active species is shifted towards the unmodified rhodium carbonyl with low ligand excess. Formation of the unmodified complex is suppressed when the ligand/metal ratio increases to 10.
Because of the high local ligand concentration inside a small reverse micelle, the hydroformylation reaction is mainly catalyzed by water-soluble $Rh - TPPTS$ complex even with low ligand excess under microemulsion conditions. Therefore, microemulsions allow working at lower ligand/metal ratios with respect to biphasic equivalent. The catalytic activity varies in nonlinear form as a function of the surfactant concentration of the microemulsion. The concentration of the surfactant does not have any influence on the selectivity. Therefore, it would be beneficial to determine the effect of surfactant concentration by using other substrates that enable to obtain information from the selectivities on any possible change in the active species by the addition of the surfactant.

5 Hydroformylation with Rhodium-Phosphine Modified Catalyst in a Microemulsion: Comparison of Organic and Aqueous Systems for Styrene, Cyclohexene and 1,4-diacetoxy-2-butene

5.1 Introduction

Hydroformylation reaction represents the best technology for the synthesis of aldehydes from olefins [77]. The concept of biphasic catalysis was applied to the hydroformylation first in the Ruhrchemie/Rhône-Poulenc (RCH/RP) process. The simple aqueous/hydrocarbon system provides rapid product catalyst separation. However, the application of this system is limited to low molecular mass olefins which have adequate water solubility [78]. This solubility problem can be solved by adding a suitable surfactant to the biphasic system. Reverse micelles are formed by association of polar head groups of the surfactant with colloid drops of water in an organic medium [50]. Catalytically active groups are carried by the reverse micelles and these reverse micelles act as a catalyst.

Hydroformylation of alkenes with carbon number up to 12 in microemulsion using sodium dodecyl sulfonate (SDS) and butanol has been investigated by Tinucci and Platane [79]. The use of cationic surfactant such as cetyltrimethylammomium-bromide (CTAB) has been studied in the hydroformylation of unsaturated fatty acids [59] and 1-dodecene [80][81].

In recent years, the hydroformylation of substituted olefins is gaining an importance and the applications for several valuable organic intermediates for pharmaceuticals and fine chemicals are emerging [82]. Styrene and 1,4-diacetoxy-2-butene (DAB) are important examples of these classes of substrates.

Several kinetic and mechanistic studies of the hydroformylation of styrene have been performed [83][84]. Using unmodified rhodium the detailed kinetic analysis reported that the hydrogen activation on the 4 coordinate species is the rate limiting step and product formation is accompanied by the formation of a transient species $HRh(CO)_3$ [85].

The effect of the reaction conditions on the regioselectivity in the hydroformylation of styrene has been studied by Lazzaroni et al [74]. Branched aldehyde is found as a major product and it decreases with decrease in CO or H_2 partial pressure. By means of deuterioformylation, it is showed that the regioselectivity depends on the reaction conditions. At high temperatures, β-hydride elimination of the branched alkyl intermediate forms back styrene, therefore the branched to linear ratio diminishes. However, the formation of branched and linear alkyl intermediates is irreversible at room temperature.

In another study, kinetics of hydroformylation of styrene, cyclohexene and octene using rhodium-[tris(2-tert-butyl-4-menthylphenyl)phosphite] catalyst has been reported [86].

Chaudhari and coworkers [87] have reported the kinetics of hydroformylation of styrene using $HRh(CO)(PPh_3)_3$. The rate was found independent of styrene concentration and first order with respect to catalyst concentration and hydrogen partial pressure. The activation energy was found to be 68.80 kJ mol^{-1} in a temperature range of 333 to 353 K.

In manufacturing of vitamin A hydroformylation using rhodium catalyst is a key step (cf. Figure 29). Major producers, BASF and Hoffmann-La Roche have developed processes starting from 1,4-diacetoxy-2-butene. 1,4-diacetoxy-2-butene is hydroformylated using phosphine modified rhodium catalyst to give 1,4-diacetoxy-2-formylbutane in the Hoffmann-La Roche process [88], whereas it isomerizes to 1,2 diacetoxy-3-butene at the first stage and hydroformylated using unmodified rhodium carbonyl catalyst at a high reaction temperature in the BASF process [89]. In a recent paper, kinetics of hydroformylation of 1,4-diacetoxy-2-butene using a homogeneous $HRh(CO)(PPh_3)_3$ has been studied in a temperature range of 338 to 358 K [90]. The reaction was found to be zero order with substrate concentration and first order with respect to catalyst and H_2 partial pressure.

Several analysis has been reported on hydroformylation of cyclohexene [91][92]. Kinetics of hydroformylation of cyclohexene has been studied by Marko [66] using $Rh_4(CO)_{12}$ as the catalyst precursor. Addition of the cyclohexene to the hydrido

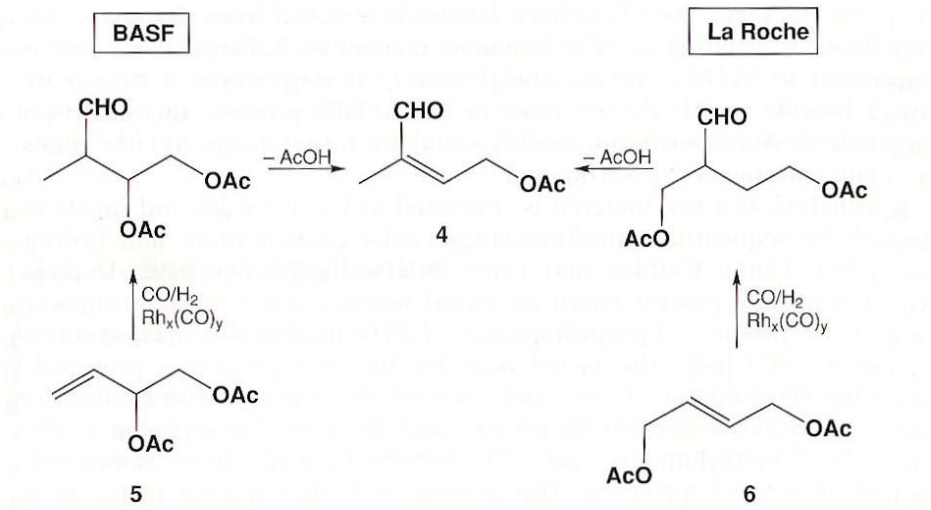

Figure 29: The hydroformylation step in the synthesis if vitamin A precursor 4.

rhodium carbonyl complex was the rate determining step under the conditions studied.

Marko et al. have also shown that reactivity at alkenes in hydroformylation followed systematic trend: Styrene > terminal alkenes > internal alkenes > cyclic alkenes.

In our ongoing work on the rhodium catalyzed hydroformylation in microemulsion medium [71], we have recently described how adding nonionic surfactant affects the hydroformylation of 1-octene in the presence of rhodium complex associated with triphenylphosphine sulfonate [93]. The active species during the hydroformylation and 1-octene in microemulsion medium have been investigated using high pressure infrared (HP-IR) spectroscopy [75].

Here, we report on the extension of the scope of microemulsion as a reaction media in the hydroformylation of long chain olefins. Thus, hydroformylation of styrene, cyclohexene and 1,2-diacetoxy-2-butene have been studied using microemulsion stabilized by nonionic surfactant. In addition, all the organic reactants were also tested under homogeneous and biphasic conditions.

5.2 Experimental

5.2.1 Materials

Rhodium dicarbonyl acetylacetonate $Rh(acac)(CO)_2$ (Sigma-Aldrich), and 30.7 wt.% aqueous solution of tris-(3-sulfophenyl)-phosphine trisodium salt ($TPPTS$) were used as received without further purification. The substrates styrene and cyclohexene were purchased from Sigma-Aldrich and 1,4-diacetoxy-2-butene was purchased from Narchem Cor. in its highest purity available. The technical grade surfactant Marlipal O13/70 (alkylpolyglycolether derived via ethoxylation of isodecanol), syngas (CO/H_2 1:1) were from Condea Chemicals and Messer Griesheim, respectively.

5.2.2 Experimental Procedure

Hydroformylation experiments were carried out in a 100 ml autoclave supplied by Premex. Preparation of the reaction mixtures, details of the experimental set-up and procedure were identical as described earlier [93].

Standard experiments were carried out at syngas pressure of 60 bar and temperature of 85 $^{\circ}C$. Composition of the microemulsion was 79 wt.% of alkene, 13 wt.% of surfactant and 8 wt.% of aqueous catalyst solution. The rhodium concentration of the reaction mixtures was 200 ppm with respect to the substrate. The analysis of the products and the reactants were carried out by gas chromatography (Sichromat 3 with Rtx-5MS capillary column). Reproducibility of all the experiments was checked by at least one duplicate experiment in order to gain confidence.

5.3 Results and Discussion

5.3.1 Hydroformylation of Styrene

In preliminary experiments, the material balance was examined using $Rh-TPPTS$ complex in microemulsion medium at standard reaction conditions (L/M=4). The products formed were 2-phenyl-propionaldehyde and 3-phenyl-propionaldehyde under the condition studied (see Figure 30). No hydrogenation or isomerization products were observed.

For the comparison of the performance of the microemulsion, the organic reactant

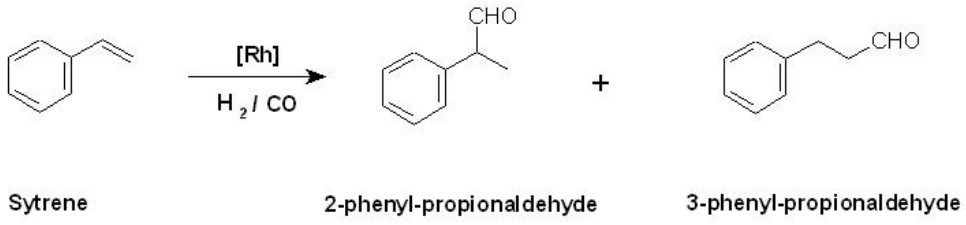

Figure 30: Reaction scheme for hydroformylation of styrene.

was also tested under homogeneous and biphasic conditions. Thus, styrene was hydroformylated using unmodified rhodium $HRh(CO)_4$ and $HRh(CO)(PPh_3)_3$ catalysts in homogeneous system and using $Rh-TPPTS$ complex in two phase system and in association with co-solvent. Aldehyde selectivities (b/n) and initial catalytic activities, i.e. mol of substrate transformed per mol of catalyst per minute at 10-20 % conversion, are summarized in Table 3.

Table 3: Hydroformylation reaction of styrene.

Catalytic System	Ligand	L/M[a]	Time(min)[b]	r_o^c	b/n[d]
Unmodified	-	-	119	69.8	1.60
Homogeneous	TPP	4	67	82.7	3.20
Biphasic	TPPTS	4	450	34.0	1.74
With co-solvent	TPPTS	4	116	70.2	1.63
Microemulsion	TPPTS	4	1440	10.0	2.13
Microemulsion	TPPTS	10	1440	2.1	3.66
Homogeneous	TPP	10	45	124.9	8.54
Biphasic	TPPTS	10	*	*	*

* no reaction.
a: ligand per metal ratio.
b: optimized reaction time for total conversion except for microemulsion L/M 4 : 94.1 % con. ; microemulsion L/M 10 : 2.8 % con.
c: initial activity; mol of substrate transformed per mol of catalyst per minute.
d: ratio of branched to linear aldehyde.

First, the reactions were performed at ligand metal ratio of 4. Regioselectivities are directed towards the formation of the branched aldehyde for the all catalytic systems. Preference of styrene to form branched aldehyde has been suggested by several authors [94] [95].

Under homogeneous conditions (unmodified, TPP modified), catalytic activities ap-

pear to be quite high as expected. The initial catalytic activity and more noteworthy the selectivity of the system is improved as the catalyst is changed from unmodified rhodium carbonyl $HRh(CO)_4$ to $HRh(CO)(PPh_3)_3$. The catalytic activity of biphasic system is somewhat lower than analogous reactions under homogenous conditions due to low solubility of styrene in water phase. However, the activity is still higher than expected for $Rh-TPPTS$ complex in two phase system. Moreover, the selectivity under biphasic condition is almost equal that is observed for unmodified rhodium. These results indicate that unmodified rhodium carbonyl complex $HRh(CO)_3$ which is formed by loosing the ligand is the predominant species under biphasic condition with ligand/metal ratio of 4.

Addition of the co-solvent to the biphasic system leads to an enhancement of the catalytic activity, but more note worthy, to a decrease in the selectivity toward the branched aldehyde. As known, the unmodified rhodium complex is organic soluble and leads to high rates and low selectivities. Therefore, such an increase in activity and a decrease in selectivity can be attributed to an increase in the proportion of the unmodified rhodium carbonyl species in biphasic system by addition of the co-solvents.

Under microemulsion conditions the selectivity toward the branched aldehyde and the total conversion after 24 h was 2.13 and 94.1 %, respectively. From the selectivity point of view, the microemulsion system is slightly better than the biphasic and the unmodified systems at ligand/metal ratio of 4.

As previously indicated, it seems that the ligand/metal ratio of 4 is not sufficient to convert all the rhodium into the water soluble complex under biphasic conditions. To check this, the experiments under biphasic, microemulsion and homogeneous ($Rh-TPP$) conditions were repeated with higher ligand/metal ratio (L/M=10).

At high ligand concentration, all the rhodium species are modified by the ligand and converted into the water soluble complex. Therefore, no hydroformylation of the water insoluble substrate is observed under biphasic conditions.

Under homogeneous $HRh(CO)(PPh_3)_3$ conditions, a significant improvement is observed both in the catalytic activity and the aldehyde selectivity by increasing the

ligand/metal ratio from 4 to 10. Finally, the higher selectivity is observed along with a poor catalytic activity with higher ligand excess under microemulsion conditions. All these observation can be attributed most probably to the shift of the equilibria between various active species by the addition of more ligand.

From the reaction rates point of view, it is known that the catalytic activity varies nonlinearly as a function of phosphine concentration [76]. The activity increases as the phosphine concentration increases, it reaches to a maximum value. Further increase in the ligand concentration leads to lower rates due to the hindrance of the formation of the active species. The selectivity of the reaction is improved by increasing the phosphine concentration and it remains constant at a point where the activity has reached a maximum.

In the present system, the increase in the catalytic activity and the selectivity can be clearly seen as the ligand/metal ratio increases from 4 to 10 under homogeneous conditions ($Rh-TPP$). However, in the case of microemulsion, decrease in the catalytic activity is observed with the variation of the ligand excess from 4 to 10. Therefore, it is reasonably to state that under microemulsion conditions the decreasing trend of the catalytic activity begins at lower ligand excess with respect to homogeneous equivalent due to high local ligand concentration in the small reverse micelle. All the observations are in good accordance with the results obtained for 1-octene in our previous study [93].

5.3.2 Hydroformylation of Cyclohexene

Cyclohexene was chosen as an example of cyclic olefins in order to test the application of microemulsion as a reaction medium in the hydroformylation reaction.

As in the case of styrene, the performance of the microemulsion was compared with its monophasic and biphasic equivalents. The catalytic systems were tested with two different ligand/metal ratios, 4 and 10. Cyclohexanecarboxaldehyde and cyclohexane carboxylicacid were the products formed under the reaction conditions studied (see Figure 31).

Table 4 summarizes the results of the varying catalytic systems. As known, the

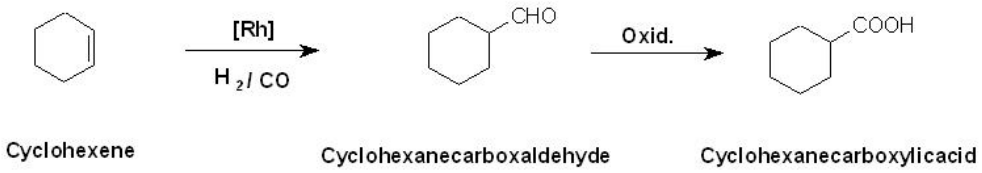

Figure 31: Reaction scheme for hydroformylation of cyclohexene.

hydroformylation of the cyclic alkenes is rather difficult due to their internal double bonds. Thus, for the all catalytic systems the observed catalytic activities are lower than the activities which were found for styrene or 1-octene. The aldehyde selectivities are grater than 99 % in all cases.

Table 4: Hydroformylation reaction of cyclohexene.

Catalytic System	Ligand	L/M^a	X$_T$(%)^b	r$_o^c$	S^d
Unmodified	-	-	100	31.1	99.8
Homogeneous	TPP	4	57.2	5.5	99.2
Biphasic	TPPTS	4	2.1	0.3	100
With co-solvent	TPPTS	4	100	8.6	100
Microemulsion	TPPTS	4	0.42	udl	100
Microemulsion	TPPTS	10	*	*	*
Homogeneous	TPP	10	33.2	3.21	99.1
Biphasic	TPPTS	10	*	*	*

* no reaction.
udl: under detection limit.
a: ligand per metal ratio.
b: total conversion after 1200 min, optimized reaction time for unmodified and associated with co-solvent system is 300 and 800 min.
c: initial activity; mol of substrate transformed per mol of catalyst per minute.
d: aldehyde selectivity, oxidation product accounts for the balance.

As expected, the highest catalytic activity is observed with unmodified rhodium carbonyl catalyst. The change of the catalyst from unmodified rhodium carbonyl $HRh(CO)_4$ to $HRh(CO)(PPh_3)_3$ and the change of the reaction medium from homogeneous to biphasic and from biphasic to microemulsion result in a systematic decrease in the catalytic activity. Moreover, in all these cases increase in the ligand/metal ratio leads to lower catalytic activities. Thus, no hydroformylation of cyclohexene is observed under biphasic and microemulsion conditions with lig-

and/metal ratio of 10. Therefore, it is reasonable to state that the unmodified rhodium carbonyl is the only active species for the hydroformylation of cyclohexene. Since only the unmodified rhodium carbonyl is the active species, the increase in the catalytic activity under biphasic conditions by addition of the co-solvent is attributed to an increase in the proportion of the unmodified rhodium carbonyl complex. This effect was also observed for the hydroformylation of the styrene as mentioned before. In the Table 5 the influence of the reaction pressure on the total conversion under biphasic conditions at the ligand /metal ratio of 4 is presented. Raising the reaction pressure causes an increase in the catalytic activity. At higher pressures the reaction seems to be further accelerated, thus, going from 60 to 100 bar the reaction proceeds faster by a factor of 132. This acceleration is probably because of the formation of unmodified rhodium carbonyl by the influence of high syngas pressure.

Table 5: Influence of syngas pressure on hydroformylation of cyclohexene.[a]

Pressure(bar)	X_T(%)	r_o^b	S^c
60	0.7	0.3	100
80	86.5	16.7	99.7
100	100	39.6	99.8

a: biphasic system, L/M 4, t=200 min.
b: initial activity; mol of substrate transformed per mol of catalyst per minute.
c: aldehyde selectivity, oxidation product accounts for the balance.

5.3.3 Hydroformylation of 1,4-diacetoxy-2-butene (DAB)

Investigation of the heterogenized catalysts can have many advantages in the hydroformylation of 1,4-diacetoxy-2-butene, because of the high boiling points and thermal instability of the corresponding aldehydes. This is the reason why we chose the substrate to test the microemulsion.

For the product identification 1,4-diacetoxy-2-butene was hydroformylated by using $HRh(CO)(PPh_3)_3$ catalyst with ligand/metal ratio of 10 at the standard reaction conditions. The major product formed was 1,4-diacetoxy-2-formyl butane (DAFB). As indicated by Chansarkar et al. [90], the elimination of the acetic acid from DAFB

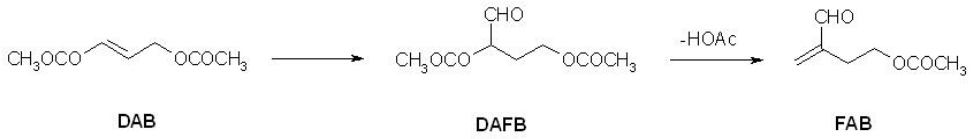

Figure 32: Involved reactions in hydroformylation of 1,4-diacetoxy-2-butene.

appeared as a side reaction. The involved reactions are presented in Figure 32. The comparison of the performance of the catalytic systems is summarized in Table 6. The use of unmodified rhodium catalyst results in isomerization of the substrate (6.2 % after 24 h). However, the hydroformylation of this isomer is not observed during the reaction. Although high reaction rates can be obtained using unmodified rhodium and $HRh(CO)(PPh_3)_3$ catalysts, the selectivities for FAB are in the range of 25-35 %. The use of biphasic system results in higher selectivity along with a poor activity. Addition of the surfactant to the biphasic system causes enhancement in the catalytic activity. However, the activity is still lower than the one that observed under homogeneous condition (both for unmodified and TPP modified rhodium). In spite of this relatively low activity, the use of microemulsion represents the best selectivity for FAB and it offers the possibility of simple catalyst recovery. Therefore, microemulsion might be a good alternative for the hydroformylation of DAB.

Table 6: Hydroformylation reaction of 1,4-diacetoxy-2-butene.[a]

Catalytic System	Ligand	L/M[b]	$X_T(\%)$[c]	$S_{DAFB}(\%)$	$S_{FAB}(\%)$
Unmodified	-	-	97.4	67.4	26.4
Homogeneous	TPP	10	95.8	66.0	33.9
Biphasic	TPPTS	10	21.4	43.1	56.9
Microemulsion	TPPTS	10	31.1	41.7	58.3

a: at standard reaction conditions, t=1440 min.
b: ligand per metal ratio.
c: total conversion of DAB

The influence of the reaction temperature and pressure on selectivity and conversion under microemulsion conditions is shown in Table 7. The effect of the temperature was investigated over a range of 60-100 $°C$. The increase in the selectivity towards

Table 7: Effect of reaction temperature and pressure on hydroformylation reaction of DAB.[a]

Pressure(bar)	Temperature($°C$)	$X_T(\%)^b$	$S_{DAFB}(\%)$	$S_{FAB}(\%)$
60	60	8.9	53.6	46.4
60	85	31.1	41.7	58.3
60	100	22.1	27.3	72.7
80	85	39.2	45.1	54.9

a: microemulsion, L/M 4, t=1440 min.
b: total conversion of DAB

deacetoxylation product (FAB) is observed at high temperatures. Drop in the catalytic activity appears as the reaction temperature increase from 85 to 100 $°C$. This surprising result is due to the change of the phase behavior of the microemulsion. Formation of the two phase microemulsion at higher temperatures can be the reason of such a decrease in the catalytic activity.

The effect of the reaction pressure is less pronounced on the FAB selectivity and the proportion of FAB decreases upon increasing syngas pressure.

Deacetoxylation of DAFB to produce FAB is only a function of temperature whereas the hydroformylation of DAB is a function of both temperature and synthesis gas pressure. Therefore at high temperatures FAB is favored but at high pressures DAFB.

5.4 Conclusions

In the all catalytic systems which were studied here the hydroformylation of styrene is somewhat faster than the hydroformylation of cyclohexene and 1,4-diacetoxy-2-butene. With the exception of unmodified rhodium carbonyl catalyst reactivity of the olefins show the following order:

styrene > 1,4-diacetoxy-2-butene > cyclohexene

When unmodified rhodium carbonyl is used as a catalyst, cyclohexene is hydroformylated faster than 1,4-diacetoxy-2-butene.

As also observed in our previous study, addition of the co-solvent to the biphasic system leads to an increase in the proportion of the unmodified rhodium species.

Therefore, use of the co-solvent results in high catalytic activity along with poor regioselectivity.

The unmodified rhodium carbonyl is found to be the only active species in the hydroformylation of cyclohexene. At high syngas pressures the equilibrium between the active species shifts towards unmodified rhodium complex. Therefore, the catalytic activity is further accelerated.

The use of microemulsion in the hydroformylation of the 1,4-diacetoxy-2-butene gives the best selectivity toward deacetoxylated product (FAB) among the catalytic systems. The selectivity for FAB increases upon increasing reaction temperature and decreasing syngas pressure.

The corresponding aldehydes of 1,4-diacetoxy-2-butene are unstable and non-volatile. Therefore, the use of microemulsion as a reaction medium might be a good alternative to homogeneous processes, because the microemulsion offers simple catalyst recovery by phase separation.

6 Rhodium Loss by Organic Phase After Phase Separation

6.1 Introduction

A general problem in homogeneous reactions is the separation of the catalyst from products after the reaction is completed. Because of high price of rhodium metal this problem becomes a critical point of rhodium catalyzed hydroformylation.

The catalyst recovery is simple and complete in aqueous phase catalysis. The principle of this technique is shown in Figure 33. Catalyst recovery can be achieved by phase separation in a decanter after the reaction. Organic products (C and D) are less polar than the aqueous catalyst solution and are therefore simple to separate from the aqueous phase in the downstream phase separator.

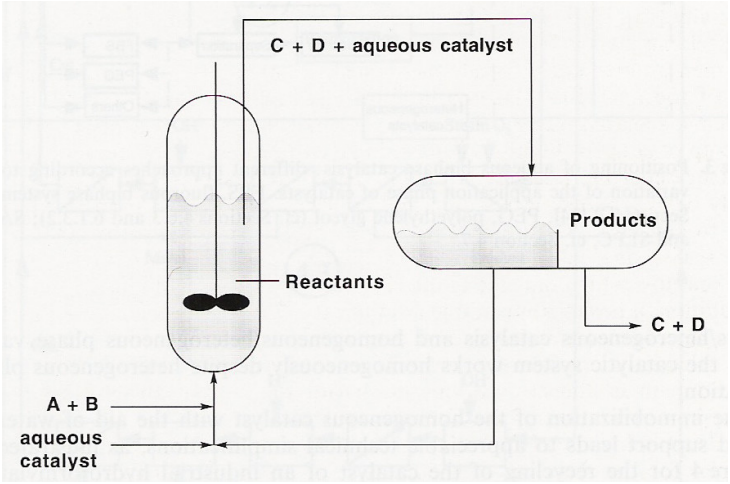

Figure 33: Principle of biphasic catalysis [78].

However, application of aqueous phase catalysis is limited with short chain alkenes which have adequate water solubility. Use of microemulsion as a reaction medium solves this solubility problem and offers simple catalyst recovery. Catalyst recovery can be achieved by phase separation as in the case of aqueous phase catalysis.

In this chapter the rhodium concentration of the organic phase after phase separation is investigated for styrene, cyclohexene and 1-octene under microemulsion conditions. For comparison purposes, rhodium content of the organic phase after phase separation for cyclohexene is also studied in biphasic system and in association

with co-solvent. Phase behavior of microemulsions for the substrates is investigated for more convenient discussion.

6.2 Experimental

Preparation procedures of the reaction mixtures was identical that described in Section 4.2.2. To simulate end of the reaction conditions (90 % conversion) organic phase of the reaction mixtures was prepared with aldehyde/alkene ratio of 9. The composition of microemulsion was 79 wt% (alkene + aldehyde) organic phase, 13 wt% surfactant (Marlipal O13/70) and 8 wt% aqueous catalyst solution. Rhodium concentration of the mixtures was 200 ppm with respect to the organic phase. Ligand/metal ratio of the mixtures was 4.

The prepared reaction mixtures were held 24 h in water bath at desired temperature in order to ensure complete phase separation. Samples were taken from the organic phase and analyzed by atomic absorption spectroscopy (Perkin Elmer 2380).

6.3 Results and Discussion

In order to get better insight into the aspect of catalyst loss by the organic phase the phase behavior of microemulsions for the substrates was studied in a temperature range of 20-85 $^{\circ}C$. Organic phase of the microemulsions was pure alkene. Figure 34 shows the phase behavior of the ternary mixture of aqueous catalyst solution, alkene and nonionic surfactant.

With octene and cyclohexene single phase regions were observed after 60 and 75 $^{\circ}C$ whereas two phase region was observed up to 85 $^{\circ}C$ with styrene. With increasing temperature single phase region might be obtained for styrene.

Rhodium content of the organic phase after phase separation was studied for 1-octene, styrene and cyclohexene under microemulsion conditions in a temperature range of 40-90 $^{\circ}C$. The results are depicted in Figure 35.

The amount of rhodium loss in the organic phase decreases at higher temperatures, when 1-octene and cyclohexene are used as the substrate. In contrast with these two substrates, an increase in the rhodium concentration is observed with styrene

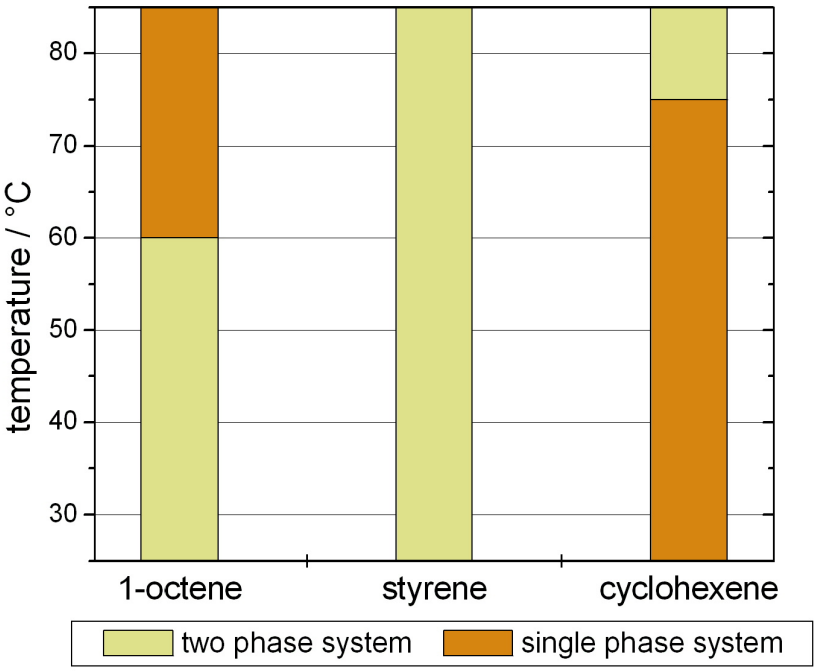

Figure 34: Phase behavior of the ternary mixture of aqueous catalyst solution, alkene and nonionic surfactant.

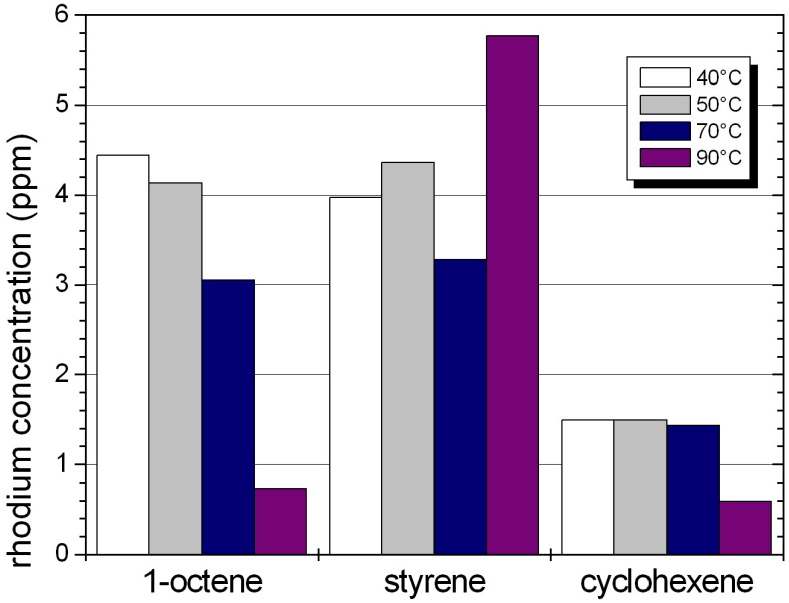

Figure 35: Rhodium content of the organic phase after phase separation in microemulsion.

as the temperature increases.

With increasing temperature two phase system turns to single phase microemulsion and lower rhodium losses are observed for 1-octene. In addition low rhodium losses are observed for cyclohexene which shows generally single phase microemulsion in the temperature range studied. It seems that use of single phase system has an advantage with respect to catalyst recovery.

Low concentration in the organic phase at 90 $^{\circ}C$ with 1-octene corresponds to that most of the rhodium is in the form of water soluble rhodium $Rh-TPPTS$ complex under these conditions. This observation corresponds well with the previous results. Although most of the rhodium in the microemulsion can be separated by simple phase separation, the determined rhodium loss (in the range of 0.6-6 ppm) is still not economically feasible. Further separation process is required accompanied by the phase separation for the complete catalyst recovery.

Rhodium content of the organic phase after phase separation was also studied in biphasic system and in association with co-solvent for cyclohexene. Comparison of the catalytic systems is shown in Figure 36.

Under biphasic and microemulsion conditions the amount of rhodium in the organic phase decreases as the temperature increases. However, strong increasing trend in the rhodium concentration is observed towards higher temperatures in association with the co-solvent. Thus, the rhodium concentration increases from 6 to 49 ppm as the temperature changes from 40 to 90 $^{\circ}C$.

It is clearly seen that addition of the co-solvent into the biphasic system results in high rhodium concentrations in the organic phase. This observation supports the previous result that the proportion of the unmodified rhodium complex which is soluble in the organic phase increases in the system with the influence of the co-solvent.

The general order of the rhodium concentration in the organic phase for cyclohexene is found as follows;

biphasic associated with co-solvent > biphasic > microemulsion

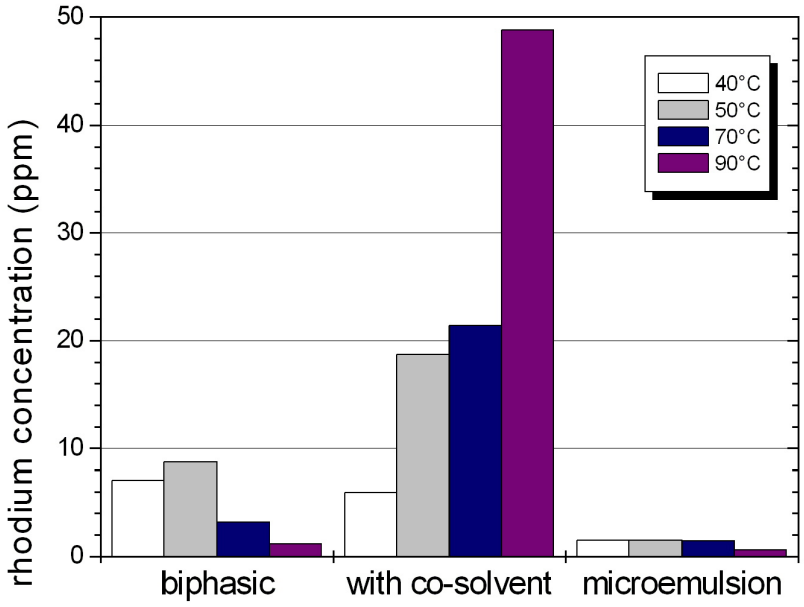

Figure 36: Rhodium loss in various catalytic systems.

This order is in good accordance with the order of the hydroformylation activity for cyclohexene. This result is completely in agreement with our previous observations. The unmodified rhodium carbonyl complex which is soluble in the organic phase was found to be only active species in the hydroformylation of cyclohexene. Therefore, highest rhodium concentration in the organic phase is expected to be in the biphasic system associated with the co-solvent which shows the highest catalytic activity.

6.4 Conclusions

Microemulsion results in low rhodium loss among the catalytic systems investigated. The rhodium concentration in the organic phase increases considerably by the addition of a co-solvent to the biphasic system. The effect of the temperature is more pronounced on the rhodium loss in the biphasic system associated with the co-solvent than in the other catalytic systems studied.

Under microemulsion conditions rhodium loss after phase separation varies between

0.6 - 6 ppm for the substrate studied. For complete catalyst recovery additional separation step is necessary.

7 Investigation into the Active Species of Rhodium Catalyzed Hydroformylation in Microemulsion

7.1 Introduction

Application of aqueous biphasic catalysis in hydroformylation solved two basic problem of classical homogeneous process successfully [9]. Separation and recycling of the catalyst are rendered easily by phase separation. However, increase in the chain length of alkene leads to low reaction rates because of poor alkene solubility in aqueous phase. Therefore, hydroformylation of long change olefins poses a serious challenge.

Several methods have been proposed to overcome this solubility problem [96][97]. Performing the reaction in a microemulsion is a useful way to increase the reaction rate in the hydroformylation of higher alkene [60][59]. Addition of suitable surfactant to the biphasic system causes a formation of microemulsion with the characteristic of large oil water interfacial area [50].

We have several studies on rhodium catalyzed hydroformylation in microemulsion medium using nonionic surfactant of alkylpolyglycolether [93][71]. We recently studied the hydroformylation of 1-octene in the presence of the rhodium complexes associated with triphenylphosphine sulfonate [98]. The combination of the experiments under comparable homogeneous and biphasic conditions was performed in order to make direct comparison of microemulsion with the classical systems.

Under biphasic conditions the observed catalytic activity at ligand/metal ratio of 4 is higher than expected for the poorly water soluble organic reagent (cf. Figure 37). It seems that at low ligand/metal ratios the equilibrium between various active species shifts towards the unmodified rhodium carbonyl that is soluble in the organic phase. As the ligand/metal ratio increase to 10 the formation of the unmodified rhodium carbonyl is suppressed. Therefore, at high ligand/metal ratios water soluble $Rh - TPPTS$ complex is the predominant species and no hydroformylation of the substrate is observed in biphasic system.

However, under microemulsion condition the concentration time profile remains

equal as the ligand/metal ration increases from 4 to 10. In addition all reactions are observed with a moderate selectivity of about 2.65. So, further investigations were necessary on the intermediates present during the reaction in order to better understand the behavior and influence of microemulsion.

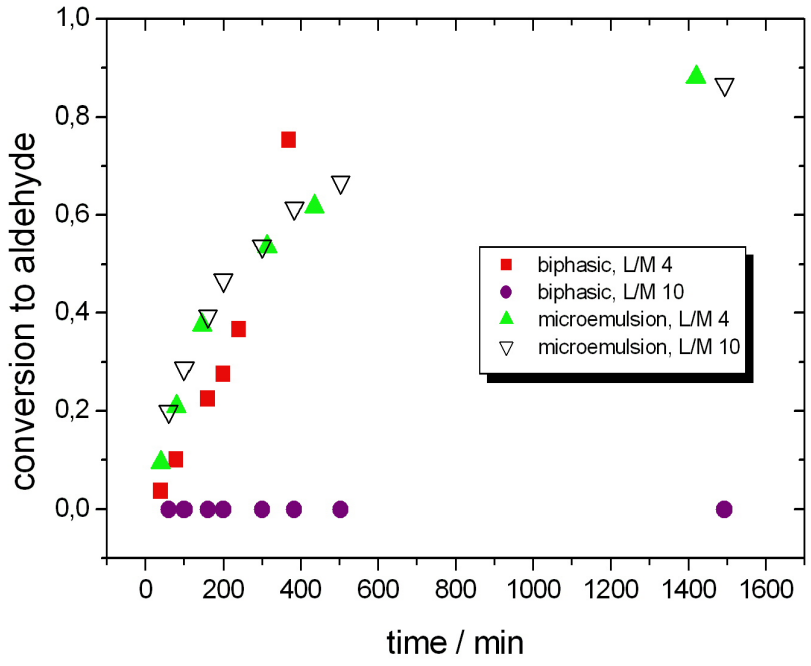

Figure 37: Hydroformylation of 1-octene under microemulsion and biphasic conditions. 85 $°C$, 60 bar, 200 ppm Rh.

As known, high pressure spectroscopic techniques are applied to identify organometallic compounds present under pressure [99][100]. In this study the formation of the various rhodium carbonyl complexes is investigated by means of high pressure infra red (HP-IR)spectroscopy.

7.2 Experimental

Rhodium dicarbonyl acteylacteonate $Rh(acac)(CO)_2$ and 1-octene were purchased from Aldrich and Fluka, respectively. 30.7 wt% aqueous solution of tris-(3-sulfophenyl)-phosphine trisodium salt ($TPPTS$) was received from Celanese. The technical grade surfactant Marlipal O13/70 (alkylpolyglycolether derived via ethoxylation of isode-

canol) was from Condea Chemicals.

All syntheses of air and moisture sensitive compounds were performed using standard Schlenk techniques under prepurified N_2 [101]. Water was purified by distillation. All other solvents were used as received. Preparation procedure of the reaction mixtures was identical that described earlier [98]. The composition of microemulsion was 79 wt% organic phase, 13 wt% surfactant and 8 wt% aqueous catalyst solution. The rhodium concentration of the mixtures was 200 ppm with respect to the organic phase.

All infrared spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer and analyzed with the Bruker OPUS-NT software (32 scans, 1 cm^{-1} resolution, Blackman-Harris 3-Term apodization). Infrared data for solution spectra of compounds 1 and 2 were collected using NaCl windows (optical path length 0.1 mm). The in situ high pressure experiments were carried out in a 55 cm^3 SS 316 autoclave equipped with a mechanical stirrer (750 rpm), a temperature, and a pressure control. The solution was pumped through a bypass, in which ZnS windows were embedded (optical path length at 25 $°C$: 0.3 mm). The appropriate amount of reaction mixture was added to the autoclave and the assembled autoclave was purged with argon (3 X), followed by syngas (3 X 60 bar). The autoclave was then pressurized at room temperature to 49 bar, resulting in a final pressure of approximately 60 bar at 85 $°C$.

7.3 Results and Discussion

Reaction of $Rh(acac)(CO)_2$ (1) with excess phosphine ligands give the $Rh(acac)(CO)L$ (L = phosphine, phosphite) [102] complex (cf. Figure 38). This is a well know reaction and numerous examples have been isolated and characterized.

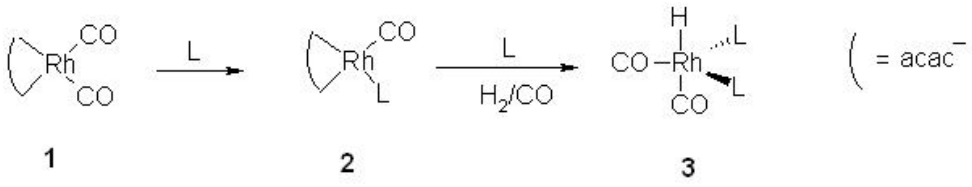

Figure 38: Reaction of $Rh(acac)(CO)_2$ with $TPPTS$ and syngas. L=$TPPTS$, TPP.

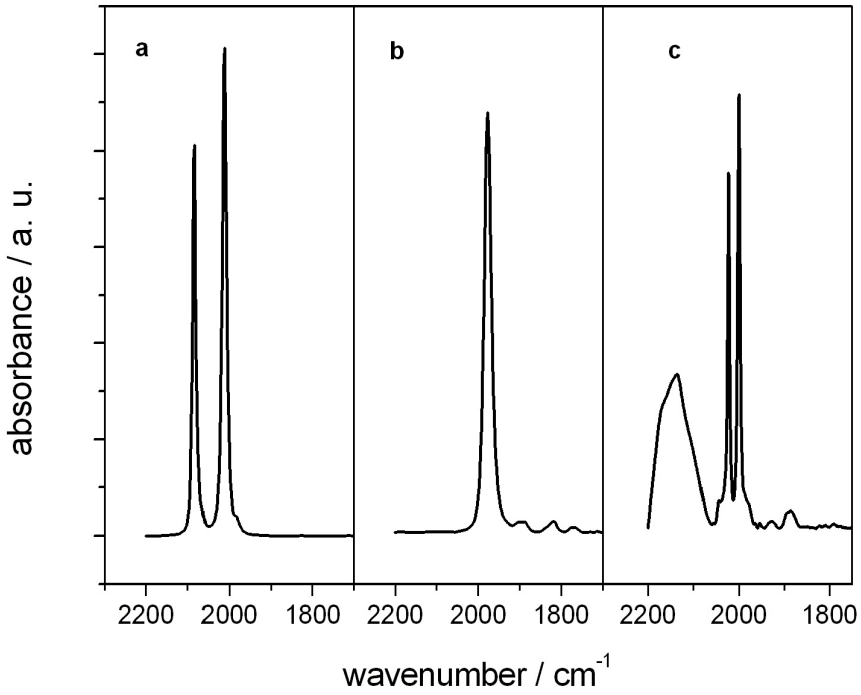

Figure 39: Spectrum of different rhodium carbonyls. a: $Rh(acac)(CO)_2$, b: TPP analogue of 2, c: TPP analogue of 3.

When reacting 1 with 4 equivalents triphenylphosphine (TPP) the expected reaction product, $Rh(acac)(CO)PPh_3$ [103] was formed as followed by IR spectroscopy (cf. Figure 39a,b). The IR absorptions of 1 (Figure 39a, at 2012 (100 %) and 2084 (80 %) cm^{-1} in CH_2Cl_2) completely disappeared and a single band for $Rh(acac)(CO)(TPP)$ appeared at 1977 cm^{-1} (Figure 39b). Addition of 1-octene, Marlipal and H_2O to this solution shifted the absorption from 1977 to 1981, 1980 and 1981 respectively, indicating that there is a small solvent effect on addition of the alkene and surfactant. When the additions were performed in a different order, to check for reaction products that might form between free CH_2OH groups of the Marlipal and the rhodium complexes, no differences in the spectra were observed.

On using a mixture of $Rh(acac)(CO)_2$ and 4 equivalents of TPP in octane, the TPP analogue of square planar compound 2 was observed. When this mixture was pressurized with syngas (CO/H_2 1:1), the formation of a different Rh(I) complex was immediately observed (Figure 39c). This compound was identified by two strong

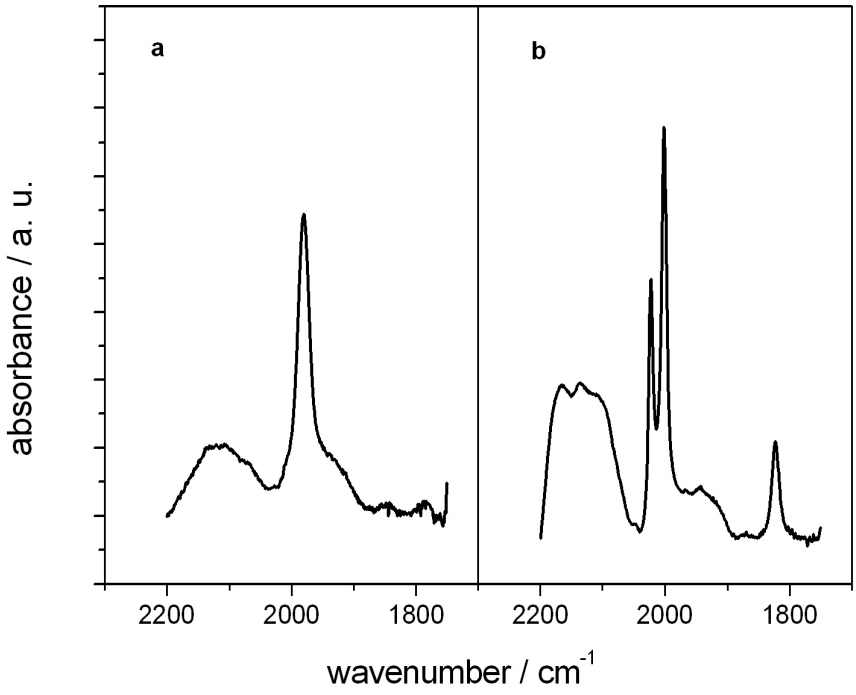

Figure 40: IR spectrum of $TPPTS$ analogue of hydride 2 (a) and 3 (b).

absorptions in the carbonyl region at 2000 and 2022 cm^{-1} (a broad CO absorption band between 2100 and 2200 was also observed). The compound formed was identified as the TPP analogue of hydride 3 [86].

On preparation of the reaction mixture ($Rh(acac)(CO)_2$ / $TPPTS$ solution / H_2O / marlipal / 1-octene) for HP-IR spectroscopy, a similar absorption (1981 cm^{-1}) was observed before pressurizing the autoclave with syngas (cf. Figure 40a). Upon flushing the autoclave with syngas (CO/H_2 1:1) and pressurizing to 49-60 bar, the absorption attributed to 2 disappeared immediately and two strong absorptions, at 1999 and 2022 cm^{-1}, as well as a weak absorption at 2044, attributed to 3 appeared (Figure 40b). Besides those two strong absorptions, an absorption at 1822 (1-octene) and a broad absorption between 2100 and 2200 (CO) were observed. The observed absorptions correspond with experiments done where the 1-octene was replaced with octane. There is no significant shift, or difference, between the spectra run on the 1-octene and the octane samples, indicating that hydride species 3 is the resting state in the catalytic cycle.

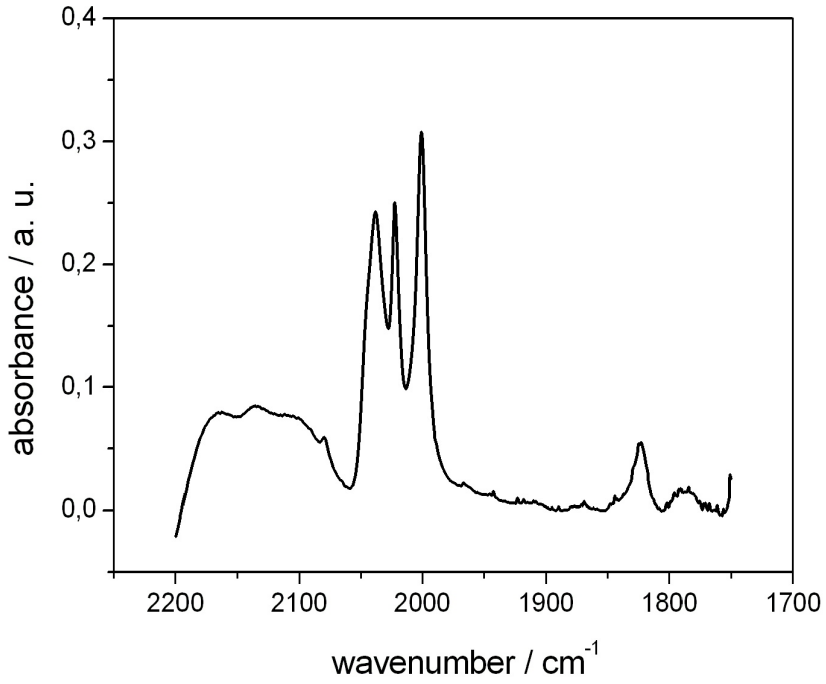

Figure 41: IR spectrum of microemulsion containing unmodified rhodium catalyst.

When the HP-IR experiment was run without ligand in the mixture (Figure 41), a fast conversion was observed from the $Rh(acac)(CO)_3$ to a different rhodium carbonyl species (1999, 2013, 2021, 2082 cm^{-1}). This second compound then gets converted slowly to the unmodified hydride (slowly means during heating of the system to 85 $°C$). At reaction temperature there are three strong absorptions observed (2000, 2022, 2038 cm^{-1}), as well as a number of weak absorptions.[1] Coincidentally two of these three absorptions overlap with the two absorptions of modified hydride 3 under reaction conditions.

The difference between the unmodified and modified hydrides can be clearly seen in the following spectrum depicted in Figure 42. When heating the $Rh(acac)(CO)_2$ precatalyst under 60 *bar* syngas to 85 $°C$ the species exhibiting three (strong) absorptions is seen to form (the absorptions that can be identified as due to $Rh(CO)_4(COR)$ can also be observed). The spectrum of this compound in the mixture of Marlipal,

[1]These weak absorptions (at 2111, 2065, 2038, 2022 cm^{-1}) were identified as due to the Rh-acyl species $Rh(CO)_4(COR)$ [92]. Weak absorptions at 2075 ($Rh_6(CO)_{16}$) and 2079 ($Rh_4(CO)_{12}$), which disappeared over time, were also observed.

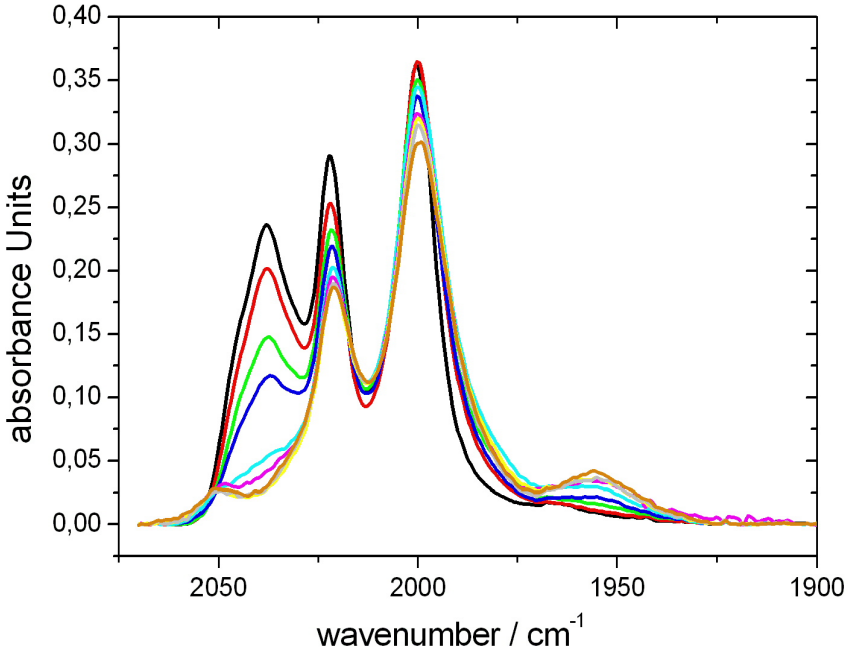

Figure 42: Addition of $TPPTS$ to a microemulsion containing unmodified rhodium catalyst. Black: begin spectrum; red: immediately after adding 1 eq. L; green: 15 min after adding 1 eq. L; blue: immediately after adding second equivalent of L; Cyan: 15 min after 2nd eq. L; etc.

water and 1-octene is given as a black line in the spectrum above. Upon addition of 1 equivalent of $TPPTS$ solution (and 0.5 ml of water), a reduction of intensity of the two absorptions at 2038 and 2022 cm^{-1} is observed. When adding a second equivalent of $TPPTS$, the absorption at 2038 completely disappears, indicating that the unmodified Rh catalyst is completely converted to the modified complex. A small shift of the peaks from 2022 to 2021 cm^{-1} and from 2000 to 1999 cm^{-1} was also observed. This shift is, with a resolution of 1 cm^{-1}, within experimental error though.

The observed conversion is rather slow which can be for the following two reasons:

1) The resting state of the unmodified catalyst is presumed to be the acyl-species $Rh(CO)_4(COR)$ (and it can indeed be observed in the spectra). This acyl-species only enters the catalytic cycle after loss of a CO ligand and subsequent insertion of a molecule of hydrogen. It is, at this

stage, not clear if the phosphine ligand can coordinate to the rhodium complex in an associative path-way.

2) Mass transport limitations in the system. The unmodified rhodium hydride is a compound very soluble in organic solvents. It is therefore reasonable to assume that the hydride is dissolved in the organic phase of the microemulsion. The $TPPTS$ ligand is a water soluble ligand and is in the aqueous phase of the microemulsion. Either of the two compounds (presumably the rhodium hydride) will have to move to the other phase of the microemulsion before it can react to form the modified hydride. This also explains why the conversion to the di-substituted hydride is exclusively observed. Upon moving from the organic phase to the aqueous phase, the $HRh(CO)_4$ will find a relatively large concentration of $TPPTS$, allowing it to react to form $HRh(CO)_2L_2$.

7.4 Conclusions

Rhodium catalyzed hydroformylation in a mixture of detergent, water and 1-octene is mainly due to modified catalysis at ligand/metal ratios of greater than 2. The resting state of the catalyst was observed by HP-IR spectroscopy, and can clearly be distinguished from the resting state in unmodified Rh catalysis in the same mixture of surfactant, water and 1-octene.

8 Summary

The shift of equilibria between various active species with varied reaction conditions seems to be a determining factor in the hydroformylation reactions.

Low ligand/metal ratios and high syngas pressure lead to the formation of unmodified rhodium carbon species with the characteristic of high reaction rates and low selectivities. In addition, it is observed that, addition of the co-solvent to the biphasic system results in an increase in the proportion of the unmodified rhodium carbonyl species with the all substrates.

The hydroformylation activity is found in the following order:

$$\text{styrene} > \text{1-octene} > \text{1,4-diacetoxy-2-butene} > \text{cyclohexene}$$

Isomerization and hydroformylation are in competition in the reaction of 1-octene. Hydroformylation of isomerization products (2-octene, 3-octene) causes a disturbance in the initial linear aldehyde selectivity. This disturbance should be taken into consideration for reliable discussions. Moreover, the initial aldehyde selectivity seems to be affected by the nature of the substrate. Hence, no considerable change is observed in the selectivity by varied reaction conditions.

In contrast with octene, influences on the selectivity can be easily observed in the hydroformylation of styrene. Therefore, use of styrene could be beneficial to test some concepts, i.e. influence of the surfactant concentration, in order to get more information.

Results obtained for the hydroformylation of octene and styrene, are in good accordance with each other. Under biphasic conditions unmodified rhodium carbonyl is the predominant species at the ligand/metal ratio of 4. Formation of this species is suppressed as the ligand/metal ratio increases to 10. However, under microemulsion condition hydroformylation is catalyzed mainly by phosphine modified water soluble rhodium complex even with low ligand/metal ratios. This is due to high local concentration of ligand inside the small reverse micelle. Although the total ligand concentrations of the reaction mixtures are same in biphasic and microemulsion system, aggregation of reverse micelles leads to higher local $TPPTS$ concentra-

tion. Therefore use of microemulsion allows working at lower ligand/metal ratios with respect to biphasic and monophasic equivalents. It is observed that addition of surfactant to biphasic system leads to an enhancement in the catalytic activity, however the activity in microemulsion is still lower that the one that observed under homogeneous conditions.

High pressure infra red (HP-IR) spectroscopic measurements were performed in order to investigate the active species under microemulsion conditions. The spectroscopic results reveal that $HRh(CO)_2(L)_2$ is the resting state of the catalyst at ligand/metal ratios greater than 2.

In the hydroformylation of cyclohexene the unmodified rhodium carbonyl complex is observed as the only active species. Therefore, $Rh-TPPTS$ complex does not show any activity under microemulsion conditions.

In the hydroformylation of 1,4-diacetoxy-2-butene highest selectivity for deacetoxylated product (FAB) with average activity is observed under microemulsion conditions among the catalytic systems. Use of microemulsion may have an advantage in practical applications because of its high boiling and thermally unstable products.

Rhodium losses by organic phase after phase separation was observed under biphasic and microemulsion conditions. Use of microemulsion results in lower rhodium loss in a range of 0.6-6 *ppm*. It is still high for industrial applications and additional separation step is necessary for complete catalyst recovery.

9 Outlook

Use of microemulsion as a reaction media in the hydroformylation of 1-octene results in high reaction rates. However in the case of styrene the rates are poor. This may due to low reactivity of water soluble $Rh - TPPTS$ catalyst. For the hydroformylation of cyclohexene the unmodified rhodium carbonyl complex is the only active species and no activity is observed under microemulsion conditions.

Higher reaction rates might be achieved by using different water-soluble ligands. Herrmann and co-workers introduced water-soluble ligands such as BISBIS bis-[phenyl (sulfonatophenyl)phosphinomethyl]disulfonatobiphenyl, 1; NORBOS tris-(sulfonato- phenyl)dimethylphosphanorbornadien, 2; and BINAS bis[disulfonato-phenylphosphi- nomethyl]tetrasulfonatobinaphthene, 3. High activity and selectivity were achieved using these ligands in comparison to $TPPTS$ in the biphasic Rh-catalyzed hydroformylation of propene (Figure 43) [104].

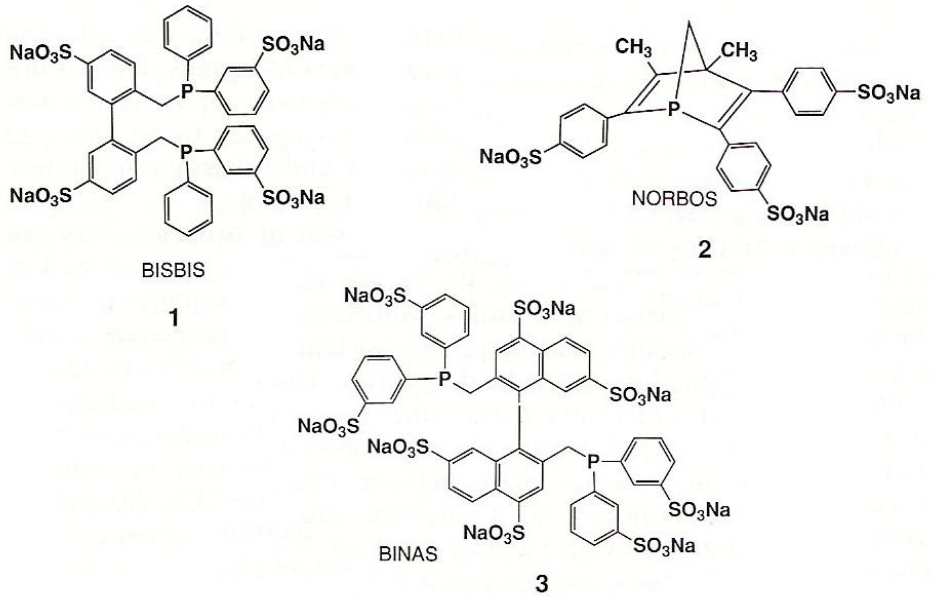

Figure 43: Different ligands for biphasic Rh catalyzed hydroformylation.

Use of these water-soluble ligands under microemulsion conditions might be beneficial especially in the hydroformylation of internal and cyclic alkenes.

An important aspect for industrial application is the complete recovery of the cat-

alyst. Rhodium loss by organic phase after phase separation is in a range of 0.6-6 *ppm* in microemulsion, therefore additional separation step is necessary for the total recovery of the expensive catalyst. Since basic task of separating catalyst from product has already be achieved by the phase separation additional membrane processes can enhance further work-up of the homogeneous catalyst.

The reverse micellar solution can be filtered using an ultrafiltration membrane to reject the aggregates containing water soluble rhodium catalyst. Use of asymmetric polyamide [105] and ceramic [106] membranes were investigated in the ultrafiltration of surfactant.

10 Nomenclature

α	mass fraction of oil in microemulsion
AAS	Atomic Absorption Spectroscopy
acac	acetylacetonate
ADH	alcohol dehydrogenase
AG	Aktiengeselschaft (incorporated company)
BASF	Badische Anilin und Soda Fabrik
BINAS	bis[disulfonatophenylphosphi- nomethyl]tetrasulfonatobinaphthene
BISBIS	bis-[phenyl (sulfonatophenyl)phosphinomethyl]disulfonatobiphenyl
BP	British Petroleum
cμ c	critical microemulsion concentration
CO	carbonmonoxide
conc.	concentration
CTAB	cetyltrimethylammomium-bromide
d$micelle$	diameter of micelle
DAB	1,4-diacetoxy-2-butene
DAFB	1,4-diacetoxy-2-formyl butane
DOP	dioctyl phatalate
FAB	formyl acetoxy butane
FID	flame ionization detector
FTIR	Fourier Transform Infrared Spectroscopy
γ	mass fraction of surfactant in microemulsion
g	specific factor of a system
GC	Gas Chromatography
GC-MS	Gas Chromatography with Mass Spectroscopy
H_2	hydrogen
HP	Hewlett Packard
HP-IR	High Pressure Infra Red Spectroscopy
IR	Infra Red Spectroscopy
L	Ligand
L/M	Ligand to Metal ratio
LPO	low pressure oxo
m_{oil}	mass of oil
$m_{surfactant}$	mass of surfactant
m_{water}	mass of water
$n_{surfactant}$	mole of surfactant
n_{water}	mole of water
n/b	normal to branched aldehyde ratio
NORBOS	tris(sulfonato- phenyl)dimethylphosphanorbornadien

o/w	oil in water type microemulsion
P	Phosphorous
PIT	phase inversion temperature
ppm	part per million
PVC	poly vinyl chloride
RCH/RP	Ruhrchemie/Rhone-Poulenc
rel.	relative
Rh	rhodium
SDS	sodium dodecyl sulfonate
Shell	Royal Dutch Shell Inc.
T	Temperature
Temp.	Temperature
TPP	triphenylphosphine
TPPTS	tris-3-sulphophenyl-phosphine trissodiumsalt
UCC	Union Carbide Corporation
w_0	molar ratio of water to surfactant
w/o	water in oil type microemulsion

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A Appendix

Table 8: Composition of applied microemulsions in different surfactant concentrations

Surfactant wt. %	Surfactant / gr	Catalyst solution / gr	Alkene / gr
0,25	0,0775	2,4	28,52
0,5	0,156	2,4	28,4
1	0,31	2,4	28,29
3	0,93	2,4	27,67
13	3,9	2,4	24,7

Table 9: Catalyst compositions. Variation of ligand excess at 200 ppm rhodium concentration

L/M Ratio	Rh(CO)2acac / mg	TPPTS(aq) solution / mg	TPP / mg
4	13	365,77	51,8
10	13	914,43	129,49
20	13	1828,78	259
40	13	3606,98	-

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